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THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT CRYSTALS OF POTASSIUM CHLORATE

By Sir C. V. Raman and D. Krishnamurti

(From the Raman Research Institute, Bangalore-6)

Received September 20, 1953

1. Introduction

The iridescent crystals of potassium chlorate which exhibit monochromatic extinctions and reflections form admirable material for a study of the optical behaviour of regularly stratified media. The fact that we had at our disposal a fine collection of these crystals led us to undertake a thorough study of the phenomena which they exhibit, and this brought to light a feature of importance which had been overlooked by the earlier investigators in the field, *viz.*, the variation of the spectral character of the iridescent reflections with the azimuth of the plane of incidence, and also revealed the existence of discrete polarised components in the spectra of such reflections. Our findings were reported in a memoir published in the November 1952 issue of these *Proceedings*. Shortly afterwards we found it possible to develop theoretical considerations which satisfactorily accounted for the facts. These, together with some further experimental results, were published in the following issue of the same *Proceedings*. A summarising article also appeared in *Current Science* for December 1952.

Fresh developments have since resulted from further investigations undertaken by us. The most striking of the new results which we wish to report in the present paper is the discovery of *the geometric patterns of reflection and extinction* which iridescent crystals of potassium chlorate exhibit when an extended source of monochromatic light is viewed by reflection at or transmission through the crystals. Typical examples of such patterns are reproduced in Figs. 3 to 10 in Plate XIX and Plate XX accompanying the paper. They show at a glance the whole group of phenomena reported in our earlier papers. Two further topics of interest are also dealt with in the present paper. A study of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope with monochromatic light reveals a rich variety of forms which are of interest in themselves and also help to elucidate the structure of the polysynthetic twins. Finally, the paper also records the interesting fact that the

iridescent crystals of potassium chlorate function as diffraction gratings and give polarised spectra when traversed by a beam of light in a direction parallel to the composition planes of twinning.

We have thought it advisable in preparing this paper to deal with the subject in such manner that it would be intelligible even to one who had not studied our earlier publications.

2. THE STRUCTURE OF THE POLYSYNTHETIC TWINS

Potassium chlorate is a strongly birefringent crystal belonging to the holohedral class of the monoclinic system and possessing a two-fold axis of symmetry as well as a plane of symmetry normal to that axis. The crystals are usually forthcoming in tablet-shaped forms. Examination of an untwinned crystal of that form on the stage of a polarising microscope makes it evident that the faces of the tablets contain the two-fold axis of symmetry and are perpendicular to the plane of symmetry. The iridescent crystals also appear in tablet-shaped forms and similar observations made with them indicate that they are polysynthetically twinned in such manner that all the components have a common direction for the two-fold axis of symmetry and a common plane of symmetry, and further that the alternate layers of the structure are so related that they can be obtained one from the other by a rotation of 180° about the normal to the faces of the tablet.

The foregoing description of the iridescent crystals as inferred from their optical behaviour is very elegantly confirmed by the two X-ray diffraction patterns reproduced as Figs. 1 and 2 respectively in Plate XVIII, the first referring to an untwinned crystal and the latter to an iridescent tablet, the crystal in each case having been set precisely normal to the X-ray beam. We are indebted for these beautiful records to Mr. A. Jayaraman of this Institute. It will be seen that the pattern of the untwinned crystal is symmetric about a line running diagonally across the picture through its centre, and that on the other hand, the pattern of the iridescent crystal exhibits geometric symmetry about *two* directions, one of which is the same as for the untwinned crystal while the other is perpendicular to it. The number of spots seen in the pattern of the iridescent crystal is, except along the axis of two-fold symmetry of the structure, twice as large as for the untwinned crystal.

3. NATURE OF THE TWIN-PLANE REFLECTIONS

The clue to an understanding of the optical effects exhibited by the iridescent crystals is furnished by considerations regarding the intensity and state of polarisation of the light reflected at the composition planes of twinning. Such reflections cannot arise if the plane of incidence of the light

coincides with the plane of symmetry; for, the well-known optical principle of reversibility indicates that the reflection coefficients should be of opposite sign for incidence on the two sides of the boundary, whereas the structures on either side being mirror images of each other, the coefficients should necessarily be the same in both cases—contradictory assertions which are reconcilable only when the coefficient is itself zero. But the reflections would reappear, though only feebly, when the plane of incidence deviates even slightly from the plane of symmetry. Such reappearance being a consequence of a difference only in direction and not of magnitude of the optical polarisations on the two sides of the boundary, there would ensue a rotation of the plane of polarisation of the incident light through 90° in the act of reflection. In other words, a light wave polarised in the plane of incidence would be reflected as a wave polarised in a perpendicular plane; and *vice-versa*. With increasing deviation of the plane of incidence from the plane of symmetry the two streams of light with reversed polarisation thus arising would rapidly gain in intensity, while at the same time the two streams of reflected light polarised in the same manner as the components in the incident light wave, which are absent in the first instance, would come into evidence and ultimately reach a strength comparable with the reflections of the other type. Thus, there would, in general, be four streams of reflected light emerging from the crystal, two with reversed and two with normal polarisation, their relative and absolute intensities being determined by the plane of incidence as also by the angle of incidence in that plane.

4. Spectral Character of the Reflection

The considerations set forth above enable us to infer the spectral character of the integrated reflection given by the entire crystal when observed with incident white light. For any given angle of incidence, the intensity of reflection would be a maximum for the wavelength at which the reflections by the successive stratifications reinforce each other by reason of agreement in phase. Since there are, as we have seen, four reflected streams of light, there would, in general, be also four wavelengths of maximum intensity in the spectrum resulting therefrom, their positions being determined by the respective optical paths. Each principal maximum would be accompanied by a set of secondary maxima in the region of wavelengths for which the reflections by the successive stratifications only partially reinforce each other. Of the four principal maxima of intensity, two would be polarised in the normal manner and two in the reversed fashion. Their relative intensities would vary with the angle which the plane of incidence makes with the plane of symmetry. When this angle is small, there would

only be two maxima of the latter type, while if the angle is large all four would appear with comparable intensities.

It can easily be shown that when the plane of incidence is perpendicular to the plane of symmetry, the optical paths for the two streams of light which emerge after reflection with reversed polarisation would be identical irrespective of the angle of incidence; for, in such a case, considerations of symmetry permit us to exchange the paths of the incident and reflected streams of light and thereby reverse the roles which they respectively play without altering the total optical paths. It follows that two out of the four maxima of intensity of reflection would then overlap and appear in the same position of the spectrum. It can be shown further that if the alternate layers in the twinning are of equal thickness, the optical retardations for the two streams of light emerging after reflection with reversed polarisation would also be identical in all cases. There would then be three maxima of intensity at the most and not four. Thus the presence of four spectral maxima would be evidence that the alternate layers of the twinning are *not* of equal thickness; the greater their difference the wider would be the spectral separation of the components exhibiting reversed polarisation.

5. STRATIFIED MEDIA IN MONOCHROMATIC LIGHT

Instead of allowing a pencil of white light to fall upon the medium in some specified direction and viewing the transmitted or reflected light through a spectroscope, a different procedure which in some respects proves itself to be far more convenient and powerful is to allow diffuse monochromatic light to be incident on the medium simultaneously in all directions and to view the reflected or transmitted light without spectroscopic aid. It is useful in this connection to recall the well-known interferences exhibited in similar circumstances of observation by a plane-parallel glass plate, or better still, by a sheet of a birefringent crystal such as mica: interferences appear which in the case of an isotropic plate are concentric circular rings, whereas in the case of a birefringent plate two distinct sets of rings appear which to a first order of approximation are both elliptic in shape. In the case of a regularly stratified medium we are concerned with the integrated effect of the reflections by a whole series of regularly-spaced laminæ: their resultant effect would evidently be to give a total reflection in the directions along which all of them reinforce each other by reason of agreement in phase. For any particular order of interference, such directions would lie along the generators of a cone whose cross-sections would be circles if the stratified medium is isotropic, and ellipses if it is birefringent. Since as we have seen, there are four streams of reflected light arising from within the twinned

crystal of potassium chlorate, there would be four cones of total reflection of elliptic shape, two having the normal type of polarisation and two of the reversed type. Further, each cone of total reflection would have running parallel to it on either side a series of fainter cones due to the secondary maxima of interference. Likewise, in the transmitted light we would have for each order of interference, four cones of maximum extinction accompanied by their respective secondaries.

6. Geometric Patterns of Reflection and Extinction

Very simple arrangements suffice for observing the phenomena indicated above. A translucent sheet of plexiglass is illuminated from behind by a sodium vapour lamp or alternatively by a mercury arc. The crystal is held as close as possible to the observer's eye or to the lens of the camera. If the illuminated screen be viewed through the crystal, the extinction bands of the latter are seen in the field of view; with sodium light they appear as dark bands on a bright field, while with the mercury arc which is a multichromatic source the extinction bands exhibit subtraction colours. The reflection spectra of the crystal, on the other hand, appear as bright curves on a dark field. With the mercury arc, the reflection patterns for its different radiations are seen well separated from each other; even the patterns due to the two yellow rays are seen clearly resolved. With some of the crystals also, more than one set of reflection and extinction patterns is observed, evidently corresponding to different orders of interference.

A great variety of patterns could be observed visually, their angular dimensions as well as the nature of the pattern depending very much on the particular crystal employed. A characteristic feature observed in all cases is that the pattern vanishes in the symmetry plane of the crystal and is seen with maximum clearness in the perpendicular plane. Besides the primary extinction or reflection bands the secondaries accompanying them could also be seen. The simplest type of pattern and one which is frequently observed is that of two semi-circular crescents facing each other with their tips narrowing to sharp points near their terminations in the symmetry plane of the crystal.

In Plate XIX, Figs. 3 and 4, we reproduce the extinction patterns and in Figs. 5 and 6 the reflection patterns for a typical and most general case where, as will be seen from the figures, there are four principal bands. In Figs. 4 and 6 the portions of the patterns near the symmetry plane are reproduced, while Figs. 3 and 5 exhibit the portion of the pattern near the perpendicular plane. It will be seen that the two outer bands which have a more or less constant angular separation become sharper and also fade off

in intensity as we approach the symmetry plane. On the other hand, the two inner components are most widely separated and also sharper in the vicinity of the symmetry plane: they approach each other and cross at the perpendicular plane.

Of the four components of the extinction and reflection bands, two are polarised with their vibration directions parallel to the symmetry plane and two others perpendicular thereto. This state of affairs is demonstrated by the four photographs reproduced as Figs. 7, 8, 9 and 10 respectively in Plate XX, the two former referring to the extinction and the two latter to the reflection pattern of the crystal. The figures were recorded by placing a polaroid sheet between the wide-angle lens and the photographic film, the polaroid being orientated with its vibration directions respectively parallel and perpendicular to the symmetry plane. It will be seen that in each case two out of the four bands in the pattern have vanished, leaving the other two in possession of the field. It should be mentioned that the birefringence of the untwinned layers of the crystal gave no trouble as they were placed so as to face away from the camera lens while the iridescent layer faced towards it.

It should be mentioned that reflection and extinction patterns of varied character are also observed in monochromatic light using crystals in which the stratifications due to twinning are far from being regular. They are however much less conspicuous than in the case of the specimens possessing a periodic structure which exhibit intense monochromatic iridescence.

7. COMPARISON WITH THE SPECTROSCOPIC OBSERVATIONS

In the Plates illustrating our earlier papers, the spectrograms reproduced had been grouped together for each particular crystal so as to exhibit the effect of varying the angle of incidence of the light. This arrangement was not altogether satisfactory, since the effect of varying the azimuth of incidence, keeping the angle of incidence constant is much more interesting from the standpoint of optical theory. The geometric patterns of reflection and extinction observed with monochromatic light exhibit the latter effect in a very vivid manner and we have now found it possible to illustrate the same effect also with the aid of spectrograms in which the angle of incidence is kept constant while the azimuth is varied in steps.

Figs. 11, 12, 13 and 14 in Plate XXI reproduce the spectrograms of the light reflected by a particular crystal. The angle of incidence is progressively increased as we pass from one figure to the next in the series, while in each figure the angle of incidence is kept constant and the azimuth of

incidence is varied in steps, commencing from a setting nearly coinciding with the plane of symmetry and ending with one perpendicular to it. Figs. 15, 16 and 17 in Plate XXII reproduce similar sets of spectrograms for a second crystal. Fig. 18 in Plate XXII refers to a third crystal in which the spectra exhibit the effect of the change of azimuth very clearly and is of particular interest since it was the identical crystal with which the geometric reflection patterns in Figs. 5 and 6 of Plate XIX have been recorded with sodium light and their polarisation exhibited in Figs. 9 and 10 of Plate XX. Comparison of the reflection patterns observed with monochromatic light with the spectral patterns obtained with white light for various azimuths of incidence reveals a remarkably perfect concordance. The transition from a doublet near the plane of symmetry to a quartet and thence to a triplet in the perpendicular plane are shown equally well in both sets of figures. The variations in the sharpness and intensity of the components and the secondaries accompanying them are also very clearly seen in both.

We should also mention that we have made visual observations of the reflection and extinction patterns of the two other crystals whose reflection spectra have been reproduced in Plates XXI and XXII. It will be noticed that the character of the spectra recorded for these two crystals are very different in appearance. Differences of the same nature have also been observed by us in the corresponding reflection and extinction patterns.

8. The Conoscopic Patterns

The interference figures exhibited by twinned crystals in convergent polarised light are of considerable interest and are discussed in some detail in the well-known treatise of Pockels on crystal optics. The illustrations of such patterns reproduced as plates in his book appear to have been obtained by the rather artificial procedure of putting a plate of untwinned crystal on the mirror of a Norremberg's doubler; the two components of the synthetic twin thus obtained are necessarily of equal thickness. However, both simple and multiple twins of potassium chlorate are forthcoming in great variety as tablet-shaped crystals, and the material thus available is particularly well suited for such observations. All that is necessary is to mount the crystals with Canada balsam between a microscope slide and a thin cover-slip and to view the same on the stage of a polarising microscope. Two special settings of the specimen are of interest; in one setting the symmetry plane is parallel to the vibration-direction of either the polariser or the analyser, while in the other setting, it bisects the angle between them. In the former setting, a dark isogyre appears along the trace of the symmetry plane, while in the latter this is absent.

As potassium chlorate is strongly birefringent, it is desirable to use the monochromatic light furnished by a sodium vapour lamp, though some features of interest may be seen even with white light. In the observations with monochromatic light the iridescent crystals may be naturally expected to exhibit their extinction patterns superposed on the patterns due to birefringence, and we have found this to be actually the case. The configuration of the extinction patterns is not essentially altered by reason of the observations being made between crossed polaroids. But some curious features are noticeable in and around the regions where the patterns of birefringence and extinction cross each other; into a description of these features we do not propose here to enter.

The conoscopic figures of twinned potassium chlorate assume their simplest form when the crystal consists of only two components. They may then be described as a superposition of the birefringence patterns of the individual components, but as the result of such superposition two other sets of figures are also seen in the field which may be designated as the *differential and summational patterns* respectively. If the components of the twin are of equal thickness, the entire pattern is symmetrical with respect to the direction of the normal to the plate. If, on the other hand, the components are of unequal thickness, their individual patterns are naturally different, and their differentials and summationals drift away to one side and the pattern becomes unsymmetrical. In the normal setting of the crystal the differentials are very prominent, while in the diagonal setting the summationals dominate the picture. The former consist of a set of parallel lines, while the latter are closed curves approximately elliptic in shape. The differentials represent interferences of a lower order and may be seen as coloured bands in the appropriate parts of the field with incident white light. The foregoing remarks are illustrated in Plates XXIII and XXIV for four specimens numbered I, II, III and IV respectively, each in the two settings already specified. For these photographs we are indebted to Mr. T. K. Srinivasan by whom they were recorded in the course of an unpublished investigation at this Institute.

It is not to be expected that the conoscopic figures observed would always be of the comparatively simple types illustrated in Plates XXIII and XXIV. A form of pattern frequently noticed is that which resembles that of an untwinned crystal, but in which the successive bands exhibit periodic fluctuations of intensity. Four patterns of this type are reproduced in Plate XXV. These again were recorded by Mr. T. K. Srinivasan in the course of his examination of numerous specimens with a petrographic microscope. The detailed interpretation of these patterns awaits further investigation.

9. The Twinned Crystals as Diffraction Gratings

Optical theory indicates that a regularly stratified medium can in appropriate circumstances also function as a diffraction grating and exhibit the phenomena arising therefrom. Several examples could be cited as illustrations of this statement. It is therefore not without interest to record the fact that the polysynthetically twinned crystals of potassium chlorate have actually been observed by us to exhibit such effects. For this purpose it is necessary to use a crystal in which the stratifications are not excessively fine and, in order to eliminate boundary effects as far as possible, to immerse the crystal in a cell containing liquid paraffin or other suitably chosen liquid of which the refractive index approximates to the mean index of potassium chlorate. The crystal is set in the cell in such manner that a pencil of light entering the crystal at one edge and traversing it in a direction parallel to the composition planes of twinning emerges through the opposite parallel edge and is received on an observing screen. The cleavages of potassium chlorate are good and hence with the arrangements described, disturbing effects other than those arising from the lamellar structure of the crystal are not serious.

We have made observations in the manner described above with three specimens and noticed that the emergent pencil of light is spread out by diffraction over a wide range of angles on either side of the direction of the undeviated pencil. With incident white light, coloured spectra are observed, whereas with monochromatic light the field exhibits a great many interference bands with local concentrations of intensity such as would be exhibited by a diffraction grating. The most remarkable feature, however, is that the diffraction bands observed are markedly polarised but in different ways, some concentrations in the field appearing bright for one position of the polaroid while the others disappear and *vice-versa*.

In a general way an explanation of the results observed by us is not far to seek. It is evident that except in the particular case when the light traverses the crystal along the lines of intersection of the planes of the lamination with the symmetry plane of the structure, the alternate layers of the twinning present optically different orientations to the light waves traversing them. As a consequence, the two vibration directions as well as the optical paths of the light wave would be different in the alternate layers. In these circumstances the crystal would necessarily function as a phase-change diffraction grating, the resultant spectra exhibiting polarisation effects of the character observed. Since the path differences involved are fairly large, it is necessary to use incident monochromatic light in order to reveal the resulting phenomena completely.

10. SUMMARY

Iridescent crystals of potassium chlorate exhibit geometric patterns of reflection and extinction respectively when a field of diffuse monochromatic light is viewed by reflection at or transmission through the crystal. The patterns consist in general of four closed curves, two of which are polarised with their vibration directions parallel to the plane of symmetry of the crystal and the two others perpendicular thereto. The configuration of the patterns exhibits a perfect concordance with the spectral character of the reflections or extinctions observed with incident white light at corresponding azimuths of incidence and thus furnishes a complete picture of such spectral behaviour. Photographs of the geometric patterns are reproduced with the paper as also of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope. The paper also reports the observation that the twinned crystals of potassium chlorate function as diffraction gratings and give polarised spectra when light traverses them along their composition planes of twinning.

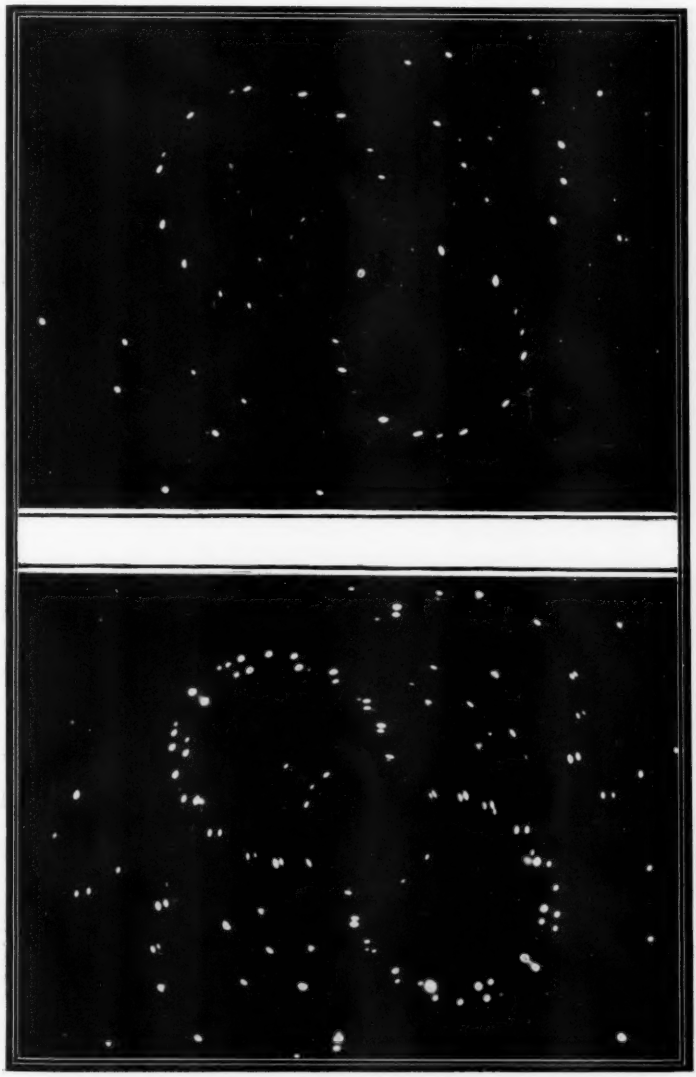


FIG. 1

FIG. 2

X-ray Diffraction by Untwinned and by Iridescent Crystals

FIG. 3

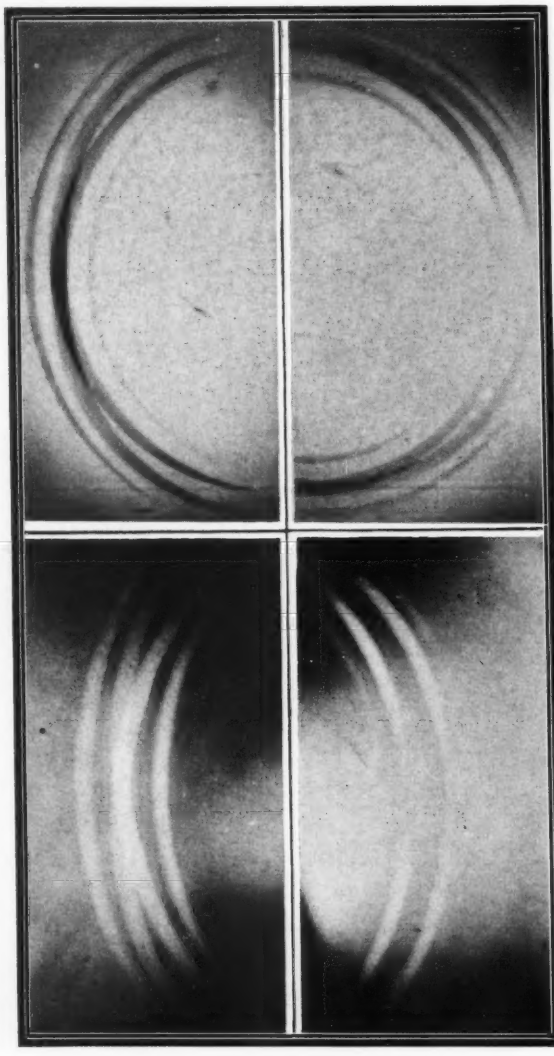


FIG. 4

FIG. 5

FIG. 6

Geometric Patterns of Extinction and Reflection

FIG. 7

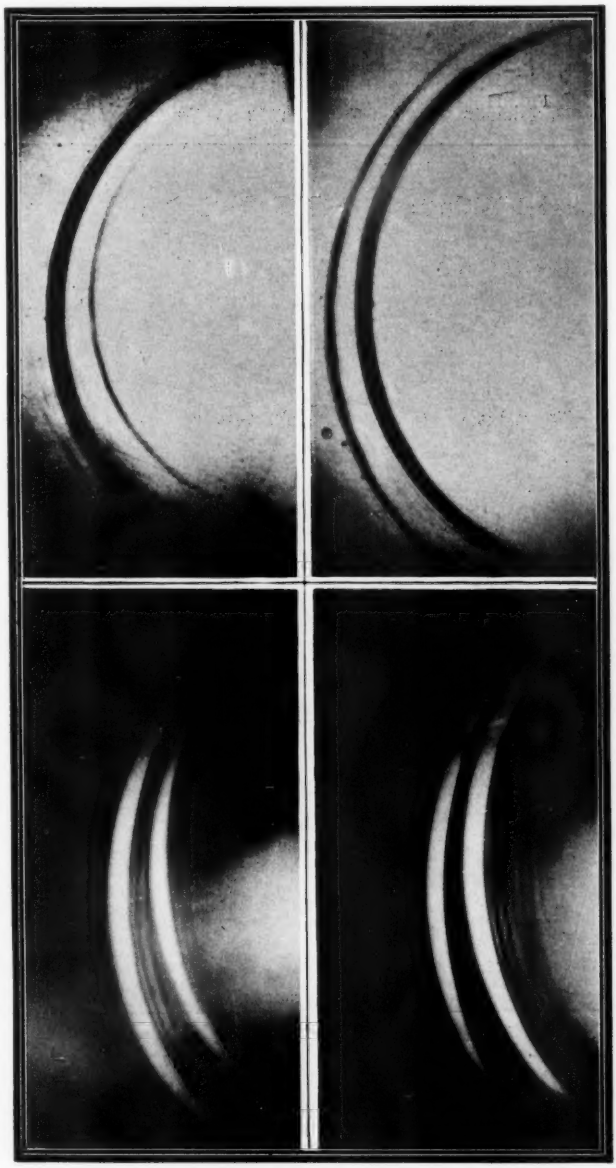


FIG. 8

FIG. 9

FIG. 10

Polarisation of the Patterns

FIG. 11 FIG. 12

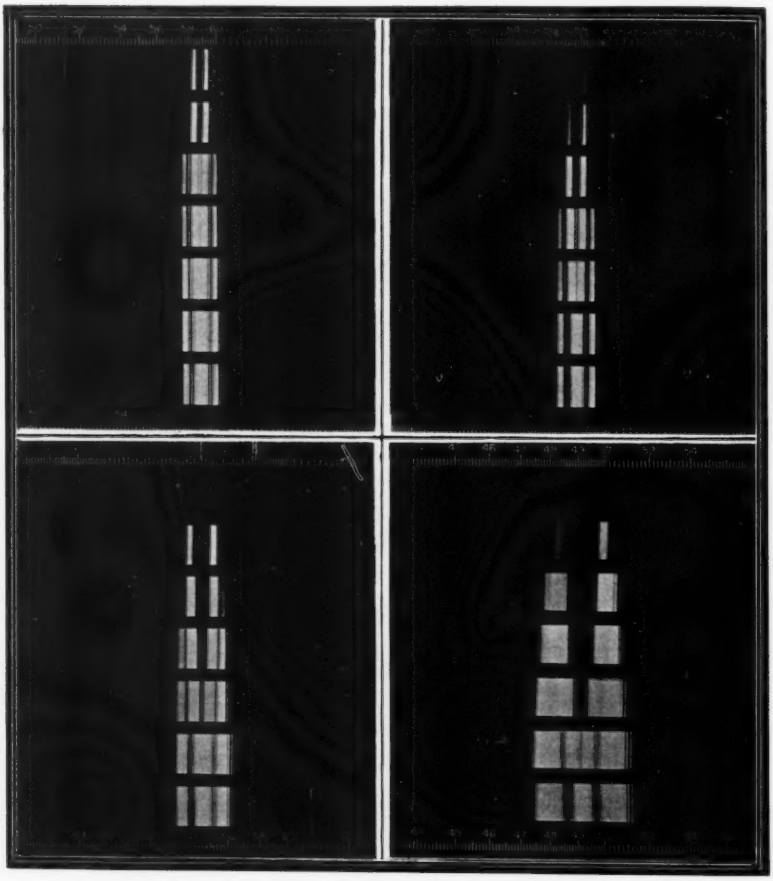


FIG. 13 FIG. 14

Reflection Spectra of Iridescent Crystals

FIG. 15

FIG. 16

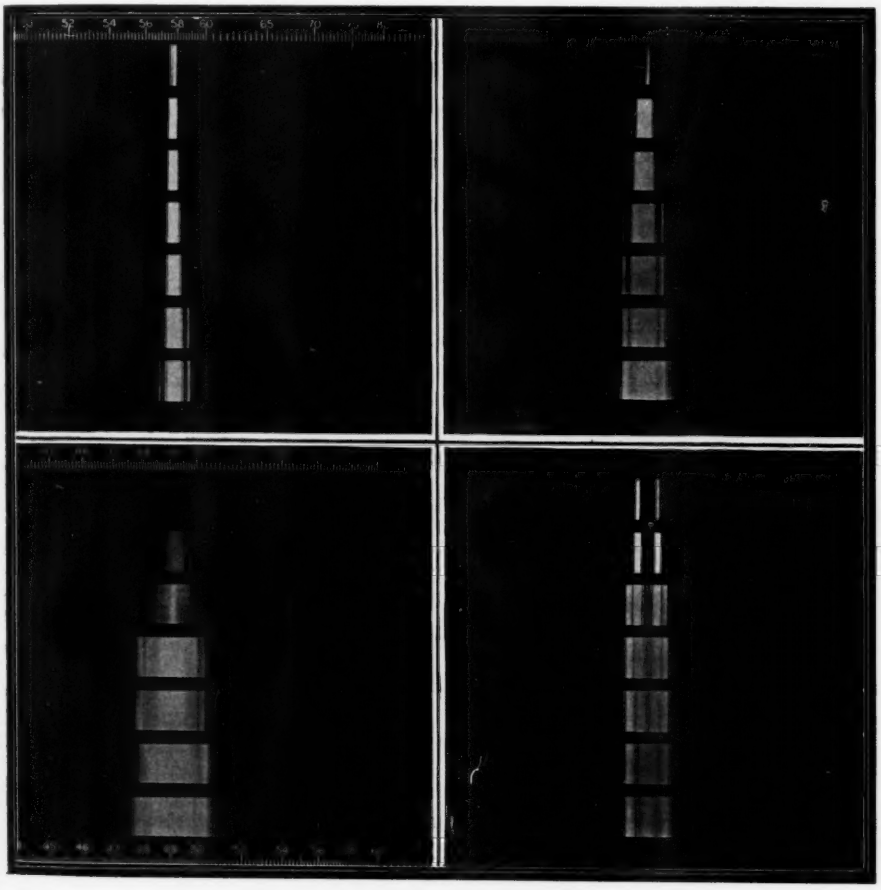
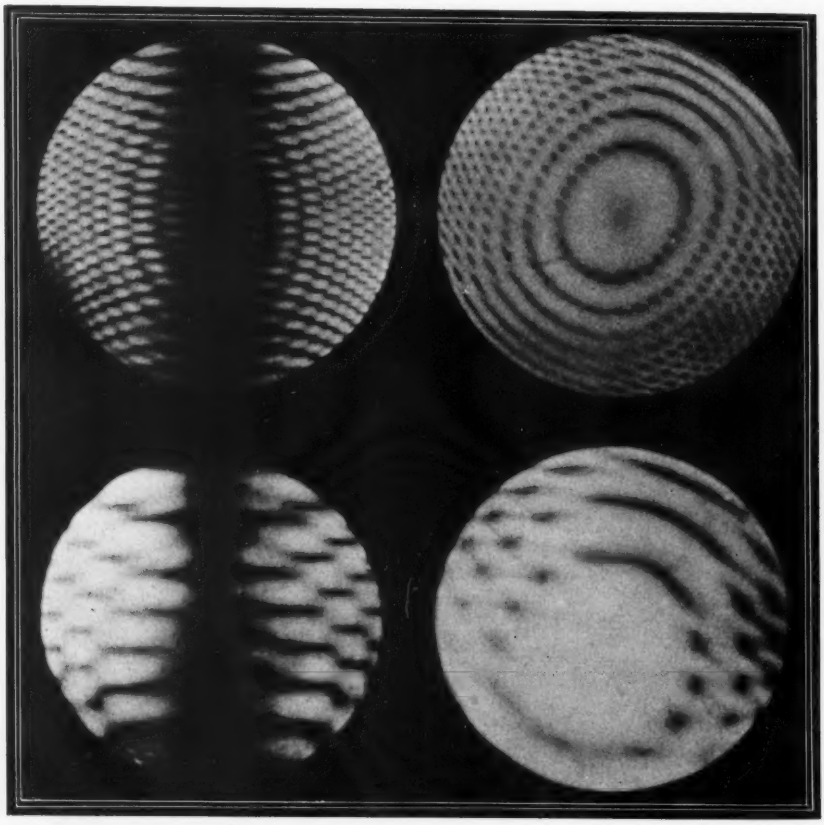


FIG. 17

FIG. 18

Reflection Spectra of Iridescent Crystals

Normal Setting Diagonal Setting

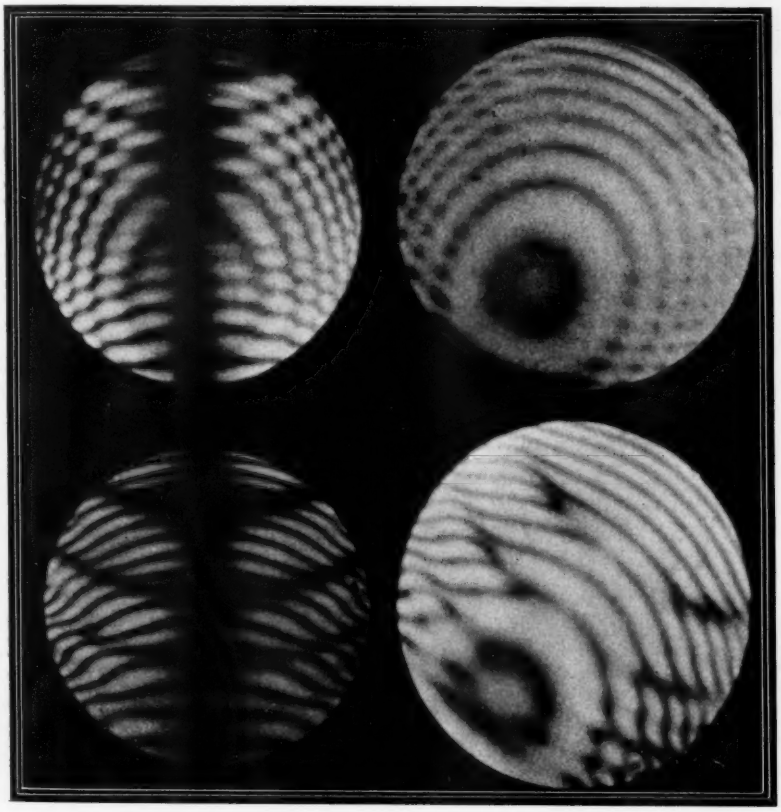


I

II

Symmetric Conoscopic Patterns

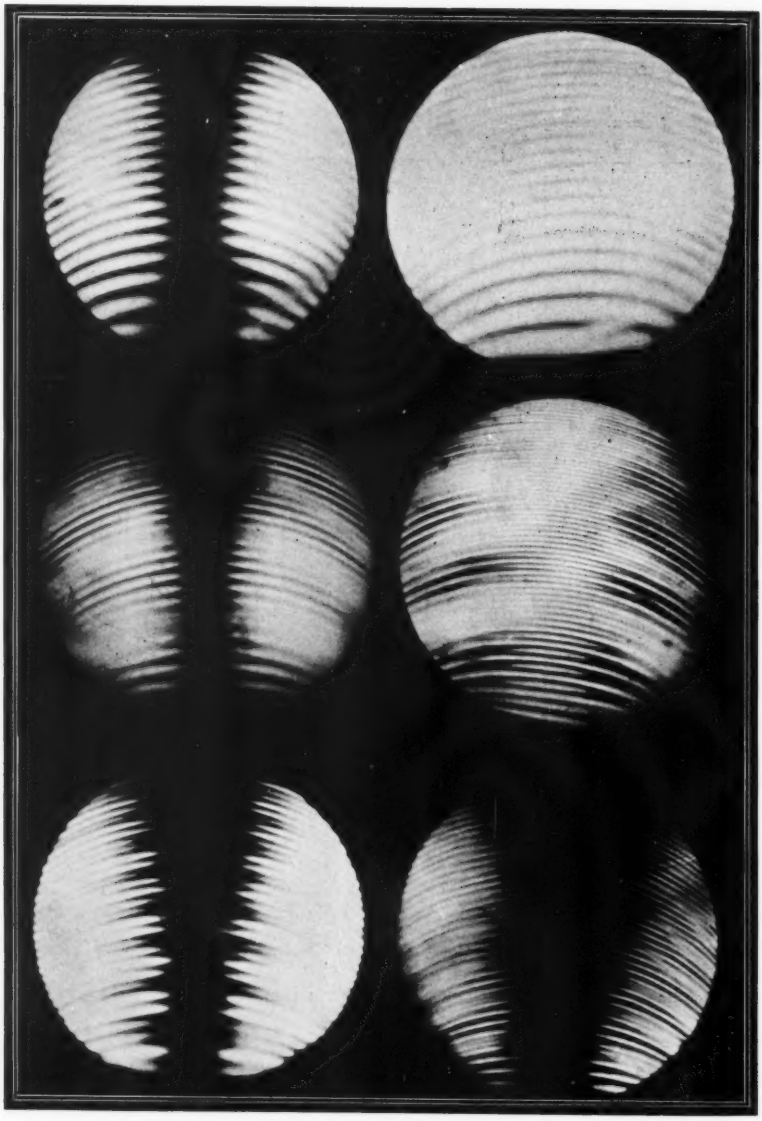
Normal Setting Diagonal Setting



III

IV

Asymmetric Conoscopic Patterns



Conoscopic Patterns of Iridescent Crystals

THIOPHENES AND THIAPYRANS

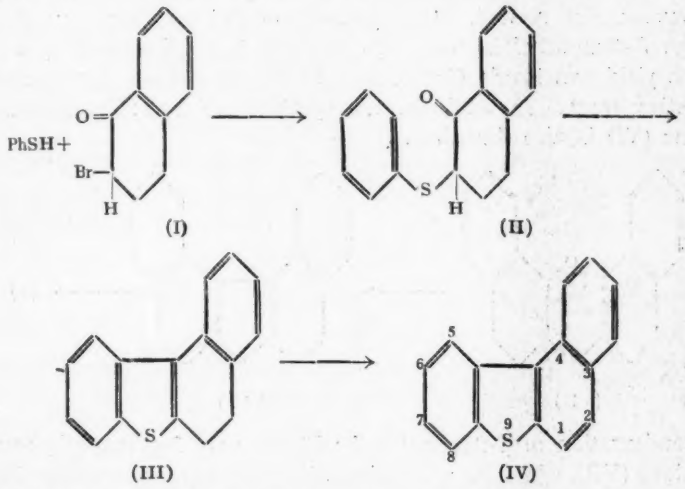
Part XI. A New Route to Polycyclic Thiophenes

BY K. RABINDRAN AND B. D. TILAK, F.A.SC.

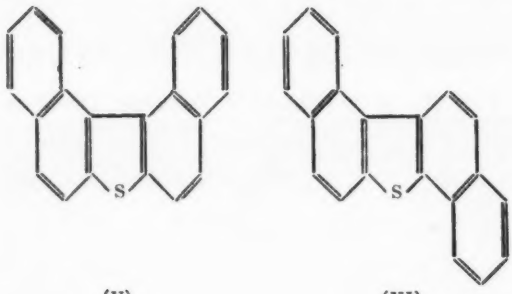
(Department of Chemical Technology, University of Bombay)

Received April 7, 1953

THE synthesis of dibenzothiophene, 1:2-benzo-9-thiafluorene and 3:4-benzo-9-thiafluorene (IV) starting from 2-bromocyclohexanone and thiophenol, α-thionaphthol and β-thionaphthol has been described in the previous communications.[1, 2] The synthesis of polycyclic thiophenes starting from aryl thiols and 2-bromo-1-tetralone (I) is now described.

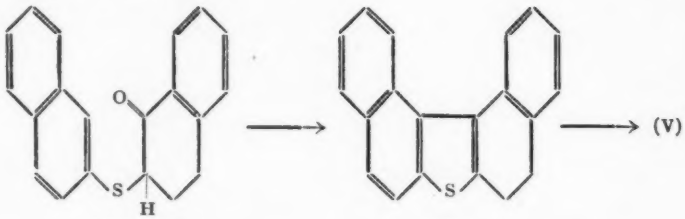


Condensation of thiophenol with (I) gave 2-phenylmercapto-1-tetralone (II) which failed to cyclize when treated with phosphorus pentoxide in boiling benzene, but underwent cyclization on heating with phosphorus pentoxide-phosphoric acid mixture under reduced pressure to give 1:2-dihydro-3:4-benzo-9-thiafluorene (III). Dehydrogenation of (III) with N-bromosuccinimide gave 3:4-benzo-9-thiafluorene (IV) which proved to be identical with the product prepared by us earlier by an alternative route.[2] Davies *et al.*[3] have recently described the synthesis of (IV) by the pyrolysis of thionaphthene-1:1-dioxide and by the hydrolytic decarboxylation of 3:4-benzo-9-thiafluorene-1:2-dicarboxylic anhydride.



(V) (VI)

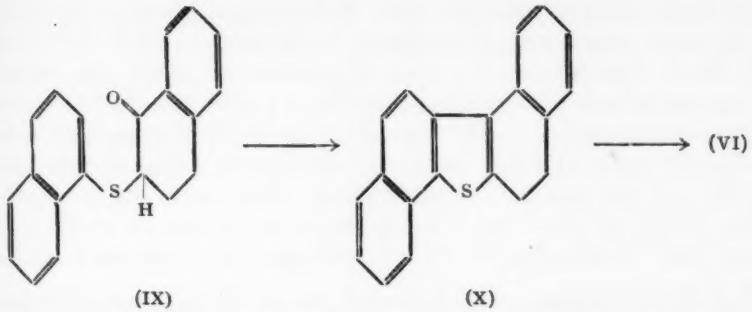
Among the different dibenzo-9-thiafluorenes only 3:4:5:6-dibenzo-9-thiafluorene (V) is known. It was prepared by Barber and Smiles[4] from 1-naphthylamine-2-sulphonic acid in five steps. The yield of the product is, however, not quoted. The synthesis of (V) starting from β-naphthol through β-dinaphthol in two steps has also been described by us earlier, but the yield was low.[5] Compound (V) has now been synthesised by an alternative route. In addition, the synthesis of 1:2:5:6-dibenzo-9-thiafluorene (VI) is also described.



(VII) (VIII)

Condensation of β-thionaphthol with (I) gave 2-(2′-naphthylmercapto)-1-tetralone (VII), which on cyclization with phosphorus pentoxide-phosphoric acid gave 1:2-dihydro-3:4:5:6-dibenzo-9-thiafluorene (VIII). The latter, on dehydrogenation with selenium, gave (V) (overall yield, 78%). Neither (V) nor (VIII) gave a picrate or a *sym*-trinitrobenzene derivative.

Starting from α-thionaphthol and (I), 1:2:5:6-dibenzo-9-thiafluorene (VI) was similarly prepared (overall yield, 76%) through 2-(1′-naphthylmercapto)-1-tetralone (IX) and 1:2: dihydro-3:4:7:8-dibenzo-9-thiafluorene (X). In contrast to (V) and (VIII), (VI) and (X) gave picrates. The cyclization of (IX) may occur in the *peri*-position but this appears unlikely in view of the β-cyclization of 2-(1′-naphthylmercapto)cyclohexanone.[2] Raney nickel desulphurization of (VI) will be studied to confirm its structure.



(IX) (X)

Compounds (V) and (VI) are thiophene isosters of 3:4:5:6-dibenzophenanthrene, and 1:2:5:6-dibenzophenanthrene. The former hydrocarbon is inactive, whereas the latter is carcinogenic.[6] Compound (V) has likewise proved inactive.[6] Compounds (V) and (VI) are also structurally related to 3:4:5:6-dibenzofluorene and 1:2:5:6-dibenzofluorene. The former fluorene derivative is inactive, whereas the latter is carcinogenic.[6] The carcinogenic activity of (VI) will be studied.

The scope and limitations of the present synthesis using 2-bromo-1-tetralone are similar to those of the new synthesis of dibenzothiophene described earlier.[1]

Experimental

2-Bromo-1-tetralone (I) was prepared according to Strauss and Rohrbadher.[7]

2-Phenylmercapto-1-tetralone (II).—2-Bromo-1-tetralone (16·4 g.) was added to a solution of thiophenol (8 g.) in 20% aqueous sodium hydroxide (14·6 c.c.) at 20–25° over 15 minutes, under stirring. After stirring for 1½ hours, the mixture was diluted with water and extracted with ether. Removal of ether gave an oil (18·1 g.), which on distillation gave a colourless liquid (15·3 g., yield 83%), b.p. 195–205° (bath temp.)/1 mm. (Found: 76·1; H. 5·5. $C_{16}H_{14}OS$ requires C, 75·6; H, 5·5%). Attempts to prepare a 2:4-dinitrophenylhydrazone or a semicarbazone from (II) were unsuccessful.

1:2-Dihydro-3:4-benzo-9-thiafluorene (III).—Compound (II) (2·7 g.) was added below the surface of a mixture of phosphorous pentoxide (11 g.) and phosphoric acid (6·5 c.c.), kept heated at 175°/1·5 mm. over 30 minutes. A little benzene was used to rinse the separating funnel through which (II) was added. After the addition, the temperature of the bath was raised to 215° and the mixture was heated at this temperature for 30 minutes. A pale

yellow liquid (0·65 g.) distilled over. The reaction mixture, on dilution with water and ether extraction, yielded a brown coloured oil (1·77 g.) (total yield, 94%). The oil that distilled over and the oil which was obtained from the phosphoric acid mixture after dilution and ether-extraction, both gave an identical picrate. The crude product, on distillation, gave a pale pink-coloured liquid (1·92 g.; yield 71%) which partly solidified on keeping; b.p. 190–95° (bath temp.)/0·6 mm. (Found: C, 81·7; H, 5·1. $C_{16}H_{12}S$ requires C, 81·4; H, 5·1%). The *picrate* gave red-brown needles from alcohol, m.p. 105–6° (Found: N, 9·1. $C_{22}H_{15}N_3O_7S$ requires N, 9·0%).

3:4-*Benzo*-9-*thiafluorene* (*IV*).—A mixture of (III) (215 mg.), N-bromosuccinimide (180 mg.), benzoyl peroxide (10 mg.) and carbon tetrachloride (20 c.c.) was refluxed for 30 minutes. Potassium acetate (3 g.) and glacial acetic acid (1 c.c.) were added and refluxing continued further for 30 minutes. The reaction mixture was diluted into aqueous sodium hydroxide and ether extracted. The ether extract was washed, dried and solvent removed. The product (202 mg., yield 95%) was sublimed at 160–80°/0·5 mm. when it gave a yellow brown product (170 mg.; yield 80%) which on crystallization from alcohol gave colourless needles, m.p. 99–100°. Admixture of the latter product with 3:4-benzo-9-thiafluorene, m.p. 102°, prepared earlier by an alternative route[2] did not show a depression in m.p. The picrates prepared from the two compounds were also identical.

2-(2′*Naphthylmercapto*)-1-*tetralone* (*VII*).—β-Thionaphthol (7·5 g.) was condensed with 2-bromo-1-tetralone (7·8 g.) as in the preparation of (II). The reaction product (12·5 g., yield 88%), isolated by extraction with benzene, on crystallization from ether, gave 2:2′-dinaphthyl disulphide as the first crop and (VII) as a second crop of crystals. The latter on recrystallization from alcohol gave colourless needles, m.p. 60–62° (Found: C, 78·5; H, 5·2. $C_{20}H_{16}OS$ requires C, 79·0; H, 5·3%).

1:2-*Dihydro*-3:4:5:6-*dibenzo*-9-*thiafluorene* (*VIII*).—A solution of (VII) (3·15 g.) in xylene (10 c.c.) was added to a mixture of phosphorous pentoxide (13 g.) and phosphoric acid (7 c.c.) at 180–90°/1 mm. during 30 minutes. The mixture was heated further for 30 minutes. Xylene distilled over during the reaction. The phosphoric acid mixture on dilution with water gave a brown product (2·9 g., yield 97%) which on crystallization from benzene-*n*-hexane gave lustrous flakes, m.p. 186–87° (Found: C, 83·9; H, 4·9. $C_{20}H_{14}S$ requires C, 83·9; H, 4·9%).

3:4:5:6-*Dibenzo*-9-*thiafluorene* (*V*).—A mixture of (VIII) (750 mg.) and selenium (250 mg.) was heated at 300–20° for 5 hours. The reaction mixture was extracted with benzene, the solution decolourized with Norit,

and concentrated. Brown coloured flakes were obtained as a first crop of crystals (225 mg., m.p. 195–97°). A second crop (137 mg.) also separated and the mother liquor was finally evaporated when it yielded brown flakes (325 mg.) (total yield 687 mg., 92%). The first crop of crystals was purified by sublimation at 200°/0·5 mm. The pale yellow flakes, which sublimed over, crystallized from benzene-*n*-hexane in pale cream coloured flakes, m.p. 206–7° (literature, 202°[4] and 209–10°[5]) undepressed when mixed with the specimen prepared earlier by us by a different route[5] (Found: C, 84·2; H, 4·2. Calc. for $C_{20}H_{12}S$: C, 84·5; H, 4·3%).

2-(1′-*Naphthylmercapto*)-1-*tetralone* (*IX*).—2 Bromo-1-tetralone (7·8 g.) was condensed with α-thionapthol (7·5 g.) as in the preparation of (VII). The reaction product (13·0 g., yield 92%) crystallized from benzene in lustrous needles, m.p. 85–87°; raised to 86–7° after recrystallization from *n*-hexane (Found: C, 78·6; H, 5·0. $C_{20}H_{16}OS$ requires C, 79·0; H, 5·3%).

1 : 2-*Dihydro*-3 : 4 : 7 : 8-*dibenzo*-9-*thiafluorene* (*X*).—Compound (IX) (2·2 g.) was cyclized by treatment with a mixture of phosphorus pentoxide (10 g.) and phosphoric acid (5 c.c.) at 180–90°/3 mm. in the same manner as (VII). Hot xylene (5 c.c.) was used as a solvent for (IX). The phosphoric acid mixture on dilution with ice-water gave a product (2·0 g., yield 96%) which was dissolved in benzene and chromatographed using activated alumina. The product gave a uniform band which showed blue fluorescence in ultra-violet light. The chromatographed product crystallized from alcohol-benzene in minute yellow plates, m.p.122–23° (Found: C, 84·3; H, 4·4. $C_{20}H_{14}S$ requires C, 83·9; H, 4·9%). The *picrate* gave brownish red needles, m.p. 142–43° from alcohol-benzene (Found: N, 8·1. $C_{26}H_{17}N_3O_7S$ requires N, 8·2%).

1 : 2 : 5 : 6-*Dibenzo*-9-*thiafluorene* (*VI*).—Compound (X) (1·0 g.) was dehydrogenated by treatment with selenium (300 mg.) as in the preparation of (V). The crude product (0·85 g., yield 86%), on crystallization from *n*-butyl alcohol, gave minute yellow plates, m.p. 162–63° [Further purification through the picrate and crystallization from *n*-butyl alcohol-ethyl alcohol gave plates, m.p. 163–64°.] (Found: C, 84·3; H, 4·6. $C_{20}H_{12}S$ requires C, 84·5; H, 4·3%). The *picrate* gave brownish red lustrous needles from alcohol-benzene, m.p. 161–62° (Found: N, 8·6; $C_{26}H_{15}N_3O_7S$ requires N, 8·2%).

SUMMARY

Polycyclic thiophenes have been prepared starting from aryl thiols and 2-bromo-1-tetralone (I). Condensation of thiophenol with (I) gave

2-(phenylmercapto)-1-tetralone, which on cyclization gave 1:2-dihydro-3:4-benzo-9-thiafluorene. Dehydrogenation of the latter gave 3:4-benzo-9-thiafluorene (overall yield 72%). Starting from β-thionaphthol and α-thionaphthol, 3:4:5:6-benzo-9-thiafluorene (V) and 1:2:5:6-dibenzo-9-thiafluorene (VI) were synthesized similarly (overall yield, 78% and 76% respectively).

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THE PREPARATION OF LARGE NUCLEAR EMULSION DETECTORS AND THEIR APPLICATION TO THE STUDY OF K-MESONS AND HYPERONS

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Abstract

A method is described for constructing out of individual sheets of nuclear emulsion a detector of large volume and stopping power which can be used for observing entire chains of successive nuclear interaction and decay processes initiated by high energy particles.

Such a detector which had been exposed for several hours in the stratosphere has proved particularly valuable for detecting K-mesons and Hyperons* and for studying their modes of production and decay.

I. Introduction

Nuclear emulsions have, during the past six years, become one of the most useful and accurate tools for studying the properties of subatomic particles and their interaction with matter. They have been especially useful in investigating the long chain of nuclear and electromagnetic interactions and successive decay processes by which the incident cosmic ray energy is first distributed among stable and unstable particles and then dissipated in the traversal of the atmosphere or other materials.

One of the main limitations of the usefulness of the nuclear emulsion technique arises from the requirement that the emulsion must be sufficiently thin to permit microscopic examination with high resolution. In practice this limits a nuclear emulsion detector to a thickness of the order of one millimeter and it is therefore rare that more than a small fraction of the chain of interaction and decay processes is observable in any particular case.

Large detectors consisting of a carefully aligned assembly of glass plates coated with nuclear emulsions have been employed since 1948.[1] In such

* The term "K-meson" designates an unstable particle whose mass is intermediate between that of the π-meson and the proton.

The term "Hyperon" designates a particle whose mass is intermediate between that of the neutron and the deuteron. This designation was suggested at the Cosmic Ray Congress held at Bagnères-de-Bigorre in July 1953.

detectors, tracks of particles which traverse the plate assembly can be traced from emulsion to emulsion through the intervening glass plates and therefore the behaviour of the particles can be observed intermittently over distances of the order of several centimeters. From the spacing of successive emulsions, and the position and orientation of a track segment in one emulsion one can predict in the succeeding emulsion an area where the continuation of the track ought to appear if the particle was not absorbed or appreciably scattered in the intervening glass plate. The correct identification of the continuation of a track or group of tracks requires, therefore, that they are clearly distinct from other tracks which traverse the predicted area.

This type of detector has proved very useful for tracing heavy primary nuclei of the cosmic radiation or groups of parallel tracks representing the core of high energy showers,[2, 3] because such tracks or configuration of tracks are clearly distinguishable from the general background; it is not however suitable for tracing fast singly charged particles or slow particles which suffer considerable scattering in the material between emulsions. It is of course also a disadvantage of such a detector that a large fraction of the particle trajectories lies in the glass backing of the emulsions and is not available for observation.

In order to overcome these limitations we have constructed a large detector consisting of emulsion only. This block of emulsion was composed of individual unbacked emulsion sheets and it was our objective to subsequently align the processed emulsions with sufficient accuracy to permit tracing the entire chains of interaction and decay processes which are initiated in the block by high energy cosmic ray particles.

The same problem has recently also been considered by Powell[4] and by Stiller *et al.*[5] and apart from minor differences in development procedure the method which we finally adopted differs mainly in the higher accuracy aimed at and achieved in the alignment of emulsion sheets after development; this we believe to be of great value in heavily exposed plates and in general in such cases where (as in the tracing of fast singly charged particles) the general background of similar tracks is fairly high.

The ideal solid emulsion detector is obviously one in which emulsion sheets exposed in a tightly packed block are subsequently, for the purpose of microscopic examination, mounted on slides in such a manner that if put on the microscope stage, the exit point of a given track in the upper emulsion coincides with the entrance point in the next. This ideal superposition over an entire slide has not been achieved for two reasons:—

(*a*) The emulsions even when tightly packed for exposure are not flat and gaps between adjoining surfaces vary from zero to about 0·15 mm. Thus the exit and entrance points do not coincide but rather are separated by an unknown distance along the direction of the track (this distance is smaller the steeper the track).

(*b*) Since in the method which we finally adopted the emulsion is mounted on glass *before development*, distortion moves the exit point on the air surface from its proper position such that exit and entrance points cannot simultaneously be aligned for all tracks.

An emulsion block satisfactory for all purposes would be one in which the two points lie along the line of the track with an error of not more than 10–15 μ. If such alignment can be achieved, even minimum tracks in a heavily exposed plate can be traced through many emulsions, high magnification can be used for observation and no acceptable alternatives for the true continuation will present themselves. It must be remembered that if in a track passing ~ 20 emulsion sheets, possible alternatives present themselves only once or twice the work of following becomes very laborious indeed.

In our stack we have achieved a line up with an error of $\sim 50\,\mu$. This error is mainly due to distortion. It makes it possible to trace any particle whose track is heavier than minimum without any uncertainty or delay. The tracing of minimum particles however is still difficult. If the track is too steep the background in a circle of 50 μ radius is often too high to make a definite assignment. If the track is very flat the entrance and exit points are far separated along the track by an unknown amount (due to the gap between emulsion sheets) and again a number of possible alternatives present themselves. In our case a thin layer on the air surface of the emulsion is less sensitive than the remaining volume which makes the assignment of the exit point of flat minimum tracks still more difficult.

In spite of these inaccuracies which could certainly be reduced when techniques of packing and processing are improved, the block detector which we have constructed has proved very useful in locating heavy unstable particles, determining their origin, their mass and the nature of their decay products. Examples of problems for which the detector has proved superior to ordinary nuclear emulsion detectors are given in Section III.

II. Construction of an Emulsion Block Detector

Twenty-four sheets of Ilford G-5 emulsion 4″×6″ and 600 μ thick, separated by thin paper sheets, were used to construct the emulsion block. Even before exposure in the stratosphere the emulsions had been subjected to an

appreciable exposure during the air transport from England to India. We have been able to distinguish events which were recorded at airplane altitude from those which occurred in the stratosphere, because the plates were repacked just before the balloon flight. Thus when the processed plates were later lined up, only tracks which occurred during the balloon exposure could be traced from plate to plate, while pre-exposure tracks had in general no continuation in the adjacent emulsion. The assembly of emulsion sheets was placed between two bakelite plates and the resulting block was tightly wrapped with adhesive tape. The block which was finally used in our experiments was exposed in a balloon flight in September 1952 at geomagnetic latitude 19° (Delhi). The balloons reached an altitude of 90,000 feet and remained above 70,000 feet for $4\frac{3}{4}$ hours.

The requirement that the emulsions after development can be brought back accurately into the relative position which they occupied during exposure implies:—

(*a*) that two emulsion sheets which had equal overall dimensions before exposure still have equal though not necessarily the same dimensions after processing, and

(*b*) that development introduces no appreciable local distortions in the emulsions.

We have tried two different methods for obtaining a set of plates satisfying these conditions. In the first method we developed and dried the emulsion sheets before mounting them on glass plates. Here the local distortions could be kept extremely low, but the overall dimensions of the processed sheets could not be controlled with sufficient accuracy to satisfy condition (*a*).

In the second method the emulsion sheets were mounted on glass plates before processing. With this procedure we could satisfy both conditions well enough to enable us to construct a detector which is satisfactory for tracing all particle tracks whose grain density is clearly greater than minimum grain density. However, local distortions introduced during processing proved to be the limiting factor in obtaining an accuracy sufficiently high to permit the unambiguous tracing of minimum ionization tracks.

The temperature method of Dilworth *et al.*[6] was used for all developments. Processing solutions used were essentially the same as recommended by Dainton *et al.*[9]

A. *The First Method* (*The emulsions are developed and dried before being mounted on glass plates*)

Throughout the processing except during the " hot " stage each emulsion sheet was kept floating in a separate glass dish whose bottom was covered

with a sheet of paper. After the washing stage the emulsions were dried by replacing the water in the dish slowly with an alcohol-water mixture, the alcohol concentration being increased by 10% every four hours until the bath consisted of concentrated alcohol. 5% glycerine was added to the bath at the beginning of the drying process and the glycerine content was kept constant throughout.

After drying the sheets were mounted on glass plates. The detailed procedure adopted for processing, drying and mounting is discussed in Appendix I.

When treated in this manner the emulsions showed no measurable distortion. Displacements between the air and glass surfaces were less than 3μ which for plates of 600μ thickness corresponds to a distortion of less than 10 covans. Nevertheless these plates were not suitable for constructing an emulsion block detector because the emulsions which were all equal in size ($4'' \times 6''$) before processing differed by as much as 2 mm. from each other after drying. Thus the entrance and exit points of tracks in adjacent emulsions could not be brought into coincidence simultaneously in all regions of the plate.

B. *Second Method* (*The emulsions are mounted on glass plates before development*)

The procedure for mounting the undeveloped emulsions was as follows: A few drops of a solution consisting of 50% distilled water and 50% alcohol are applied to the surface of treated glass plates supplied by Ilford. These drops spread rapidly over the entire surface and swell the thin gelatine layer. The dry emulsion sheet is then placed on the glass and pressed down firmly with a hand roller. When this procedure was followed carefully, no bubbles developed in the emulsion during processing. In a later experiment with a different batch of emulsion however, we found that often bubbles formed during the late fixing stage and that application of the alcohol-water mixture with a cotton swab to the emulsion surface in addition to its application to the glass surface was a more satisfactory procedure.

Method of processing was similar to that employed by Dainton *et al.*[9] while the drying procedure was identical with that used in the first method.

In these plates local distortions were moderately large; displacement vectors of length up to 40μ were measured in various regions of the plates corresponding to distortion values up to 110 covans. Another unsatisfactory feature of this particular set of plates was a sharp drop in sensitivity towards the air surface. This effect which we encountered here for the first time has

recently been attributed by Occhialini[7] to corrosive action of fresh hypo during the late fixing stage.

C. *The Lining up of the Microscope Slides*

The plates after drying were cut into four parts yielding $2'' \times 3''$ slides, a size which is suitable for the microscope stages used in this laboratory. Next, three or four tracks of very heavy primary particles of different orientation were selected in various parts of the plate, tracks which were sufficiently prominent such that they could easily be traced from plate to plate even with the imperfect alignment which the slides presented at this state.

Then we prepared a carefully machined set of rectangular frames made of transparent plastic of $\frac{1}{8}''$ thickness; the outside dimensions of these frames were slightly larger, their inside dimensions slightly smaller than the $2'' \times 3''$ slides on which the emulsions were mounted. The first slide carrying the emulsion which formed the outside face of the block was firmly glued on to one of these frames. The next slide carrying the adjacent emulsion was glued to another frame with a slowly drying cement; its position could, therefore, be adjusted slightly for about 30 minutes. These 30 minutes were used to put the slide on the microscope stage and shift it in such a manner that if the first and second slide were alternately put into the slide holder, each of the previously selected track segments in one plate represented an exact continuation of the corresponding track segments in previous plate. After the second slide was correctly placed the same procedure was used for gluing the third slide to its frame. In this manner all slides were mounted on frames. With some practice it is then possible to mount the slides such that their relative position in the slide holder is within 10μ the same as the relative position they occupied during exposure. This error is, therefore, small compared to the about four times larger misalignment of track segments arising from distortions in the emulsion.

Although our procedure for lining up the plates was somewhat laborious, and required practice we feel that the effort spent on obtaining this relatively high accuracy was amply justified by the rapidity and confidence with which tracks could later be traced through the block. The complete assembly of emulsions lined up to reproduce the relative position they occupied during exposure we shall call an *Emulsion Block Detector.*

III. On the Application of Emulsion Block Detectors to the Study of Unstable Particles

Once such a detector has been constructed it offers many advantages over the conventional detectors consisting of single nuclear plates or of an

assembly of nuclear plates. Details of the experimental results which have been obtained so far are given in the separate papers listed in the footnote.† Here we confine ourselves to mentioning some of the investigations for which such a detector is particularly well suited.

(a) Investigations of the origin and the properties of slow K-mesons and Hyperons

It is well known that charged and neutral K-mesons exist which decay in such a way that at least one of the decay products is a charged π-meson. Well established among these are the τ-mesons ($\tau \rightarrow 3\pi$) and a neutral particle which has been variously designated by the symbols v°, V_2° and V_4° and for which the symbol θ° has recently been suggested ($\theta^\circ \rightarrow \pi^+ + \pi^-$). There is also at least one Hyperon (usually designated by V_1° but for which we now shall use the recently suggested symbol $\wedge^\circ$) which gives rise to a charged π-meson upon decay ($\wedge^\circ \rightarrow \pi^- + p$). Only a very small number of such particles have so far been found by scanning nuclear emulsions and often the conditions of observation did not permit accurate measurements. The emulsion block detector permits a systematic search for such particles by tracing π-mesons which come to rest in the block backwards towards their origin. Uptil now we have traced about 600 slow π-mesons. This work did not only yield information on the creation and the energy spectrum of π-mesons produced in nuclear interactions but also led to examples of the decay of τ-mesons and other unstable heavy particles.

A similar search is now in progress for rare unstable particles among whose decay products are charged slow μ-mesons, the existence of such particles being indicated by the observation of O'Ceallaigh.[8]

Once such rare particles are located either by the tracing of their decay products or by other means, the conditions of observation in an emulsion block are usually favourable for obtaining accurate measurements. Appreciable track length is usually available permitting good determination of the particle mass; furthermore, in many cases the particles themselves can be traced back to their origin in some nuclear event and therefore information is obtained on the mode of production and on the lifetime. Thus out of 14 K-mesons and charged Hyperons observed and traced by us, 11 were found to originate in some nuclear event in the emulsion block. Similarly

† (i) "Properties of Heavy Unstable Particles," D. Lal, Yash Pal & B. Peters, *Phys. Rev.* (In press).

(ii) "Observations on τ-mesons and on K-mesons giving rise to Capture Stars," D. Lal, Yash Pal & B. Peters, *Proc. Ind. Acad. Sci.* (In press).

(iii) "An Improved Method of Determining the Mass of Particles from Multiple Scattering Versus Range and its Application to the Mass of K-mesons," S. Biswas, E. C. George & B. Peters, *Proc. Ind. Acad. Sci.* (In press).

by tracing the charged decay products from the decay point on through the detector, information is frequently obtained on their mass, energy and interaction properties. Because of these favourable observational conditions it was possible to obtain improved mass values for the τ-meson, to establish definitely the existence of K-mesons which when at rest are captured by nuclei and give rise to capture stars, and to obtain an accurate Q-value for the decay of the Λ° Hyperon.

(*b*) *Study of high energy nuclear interactions*

Very large showers are easily located in an emulsion block detector. One may either trace any accidentally observed group of parallel minimum ionization tracks back to their origin or one may trace energetic heavy primary nuclei through the block. Both methods frequently lead to the location of large showers and about 8 showers with shower particle multiplicities between 40 and 150 have been located in our detector with comparatively little scanning effort. Such events are well suited for studying the interactions of fast shower particles, since many meters of integrated track length can easily be accumulated. Conditions are also favourable for determining the relative number of π°-mesons and of other interacting neutral shower particles produced in such high energy nuclear interactions.

These examples illustrate that the emulsion block detector is well suited for many investigations which cannot be undertaken or are extremely laborious with the more conventional nuclear plate arrangements.

During the exposure in the stratosphere, as well as during recovery, processing and other steps which led to the construction of our emulsion block detector, we had assistance from many sources which we gratefully acknowledge. Our special thanks are due to Mr. C. Waller of Ilford Limited, to the Department of Physics at the University of Delhi, in particular to Professor D. S. Kothari as well as to our colleagues, Mrs. S. Mitra, and Messrs. G. Friedmann, P. N. Krishnamurthy and M. S. Swami.

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APPENDIX I

Processing of Stripped Emulsions before Mounting them on Glass Plates

Distortion of emulsion during processing is due to the relative shift of the different layers. In the case of an emulsion which is processed after being mounted on a glass plate the lower surface of the emulsion is constrained to keep its size during all the operations of processing, while the other layers are shifted due to expansion and contraction of the emulsion in different stages. If these layers do not come back to their original position after the processing, the emulsion is said to be distorted, because the tracks traversing different layers will have changed their shape. It would seem that if one could process a stripped emulsion without pasting it on glass surface, the emulsion would move as a whole during the expansion and contraction processes and relative shifts of the layers could be avoided. In order to investigate the possibility of obtaining *distortion free* emulsions experiments were initiated to process emulsions without glass backing.

Processing

The strips were processed in small dishes, one in each dish. The dishes were sufficiently larger than the emulsion strips to allow for the expansion of the emulsion in the fixing and washing stages. Between the glass dish and emulsion surface a smooth stiff paper was placed during all stages of processing in order to avoid the danger of the emulsion sticking to the glass and getting distorted. The sheets must not be handled during processing.

Problem of sticking during hot stage

A glass plate was inserted below the paper sheet and the emulsion was then lifted from the dish and placed on a warm metal base. As the hot stage proceeds the emulsion becomes soft and has a tendency to stick to the paper on which it is lying. This introduces serious distortions because the places where the paper sticks are constrained to keep their position while the rest of the emulsion is changing in size. Several types of paper were tried to avoid the sticking trouble. Ultimately it was discovered that the nature of paper surface is not so important. Any paper of good strong texture is satisfactory. The important thing is to keep the temperature in the hot stage below 28° C. It was found that a temperature of 28°·5 is rather critical; the emulsion loses its jelly like structure and becomes soft. If the hot stage temperature is kept low and emulsion is not allowed to become soft, sticking does not occur.

After the hot stage the strips were directly introduced into the cold fixing bath. Change of fixing solutions was very frequent in the beginning and less so in the later stages. As the fixing takes place from both sides,

the fixing process is much faster than for mounted plates. The strips (600 μ) cleared in less than 24 hours.

Washing

Strips were washed in running water. Washing time was much shorter than needed for mounted emulsions. In washing, the strips increase by nearly 50% in their linear dimensions.

Drying

Most of the distortion in the processing of mounted emulsions is introduced in the process of drying. Drying of unbacked emulsions presents a special problem. It would be very difficult to dry such sheets in air without introducing serious distortion. We therefore dried the plates by extracting the water with alcohol. The strips were immersed in an alcohol-water mixture whose alcohol concentration was increased by 10% every 4 hours until all water had been removed. Each alcohol bath contained from 3% to 5% glycerine, which keeps the emulsion soft. The temperature of the alcohol-water mixture was kept below 10° C.

Mounting

After the strip is removed from the alcohol it is placed under slight pressure between two glossy cardboard surfaces until the alcohol is completely evaporated. Next the underside of the emulsion is coated with a thin plastic layer by painting it with a solution of Durofix‡ cement in acetone. After this layer is dry the emulsion is pasted with a commercial glue§ onto a glass plate heavily coated with gelatine.

The plastic coating was found to be necessary in order to avoid a softening of the emulsion surface by the glue which will lead to distortion. The gelatine coating on the glass plate must be heavy in order to take up the moisture contained in the glue; otherwise the evaporation of the water in the glue will raise bubbles and lift the emulsion off the glass surface.

Controlling the size of the strips

Unbacked emulsions will during different stages of processing not only alter their thickness but also change their linear dimensions. The biggest dimensions which the emulsion attains occurs during the washing stage ($1\frac{1}{2}$ times original). It was found that the maximum size attained depended on the hypo which was used. Two types of hypo were tried.

(i) Pure 40% sodium thiosulphate solution in initial stages and 40% sodium Thiosulphate solution *plus* 5% sodium sulphate after clearing.

‡ Product of The Rawplug Company Limited, Cromwell Road, London, S. W. 7.
§ Product of Camlin Limited, Bombay 28.

(ii) 40% sodium thiosulphate *plus* 3% sodium metabisulphite.

The expansion of the emulsion was smaller when the second type of fixing bath was used.

When the alcohol drying process starts, the emulsion strips become smaller till in about 70% alcohol water solution the size is almost equal to that of the strips before processing. However, the size continues to decrease as the drying proceeds. It is expected that if all the emulsions were treated exactly in the same way during processing, and treated in the same alcohol baths for drying, their final size should be exactly equal though smaller than their original size. However, it is sometimes found that two strips which have been processed together have slightly different sizes as they progress through different drying baths. It seems that their sizes can be manipulated to some extent by altering the concentration of glycerine in the drying baths. The higher the concentration of glycerine, the less will be contraction of the emulsion in the drying stage. It was also found that the contraction a strip will undergo in a bath depends on the temperature of the bath. The higher the temperature the greater the contraction. These findings coupled with the knowledge that the only way of increasing the size of a strip which has contracted too much is to put it back in a bath of greater water content, could be used to control the final size of the strips to a large extent. Nevertheless it seemed unlikely that the final dimensions could be controlled with sufficient accuracy ($\leq 0{\cdot}1$ mm.) to make such emulsion sheets useful for the construction of an emulsion block detector.

Stress release during hot stage

A series of emulsions were under observation during hot stage. Temperature of the hot stage was $\sim 28°$ C. Even though the emulsions did not stick to their base paper, some of them were seen to warp. This is believed to be due to release of stresses in the emulsion, which, being free to move on its base loses its rectangular shape. There seem to be two methods for avoiding this distortion. One of them is to work at a sufficiently low temperature [$< 20°$ C.] so that the emulsion does not become soft and the stresses remain frozen in it. The second is the method of releasing the stress of the emulsion prior to exposure, as suggested by Stiller *et al.*[5]

Some of the emulsions however, did not show any signs of warping during the hot stage. These emulsions when mounted showed very little distortion. Displacements between the air and glass surfaces were less than 3μ, which for plates of 600μ thickness corresponds to a distortion of less than 10 covans. Emulsions treated in the manner described here could be very useful for scattering measurements on high energy particles.

SYNTHESIS OF ISOCARAJURETIN HYDROCHLORIDE

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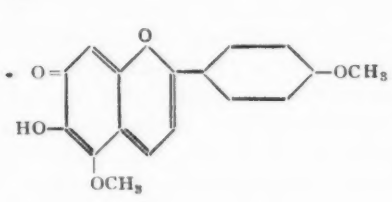
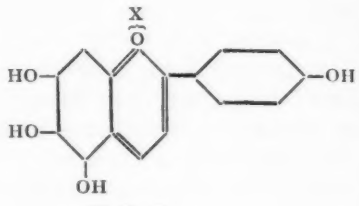
Received June 2, 1953

In an earlier publication[1] on the synthesis of carajurin, the main constituent of the cosmetic pigment 'carajura', the work of Chapman, Perkin and Robinson[2] on the constitution of carajurin was reviewed. Carajurin was considered to be the colour-base of 5:4′-dimethoxy-6:7-dihydroxy flavylium chloride (I). The most important evidence for the above constitution was derived from the demethylation of carajurin with hydriodic acid. The product, carajuretin hydriodide (II) was converted into the corresponding hydrochloride (III) which was found to be the same as scutellareinidin chloride (III).



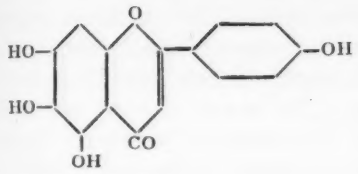
I



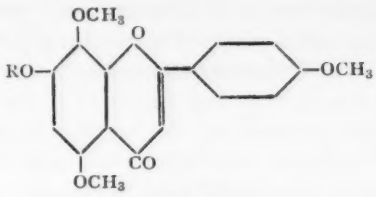
II, X=I
III, X=Cl

As we have mentioned earlier[1] the capacity of hydriodic acid to bring about isomeric change of 5:7:8-trihydroxy flavones into 5:6:7-trihydroxy compounds has an important bearing on the nature of the above demethylation. Scutellarein (IV) itself has been prepared by the demethylation of 5:8:4′-trimethoxy-7-hydroxy flavone (V *a*)[3] and 5:7:8:4′-tetramethoxy flavone (V *b*)[4]. Besides causing demethylation, hydriodic acid opens out the heterocyclic ring of the flavone molecule producing as a probable intermediate the diketone (VI). Subsequent ring closure involves the hydroxyl which forms part of the quinol unit and hence scutellarein results.

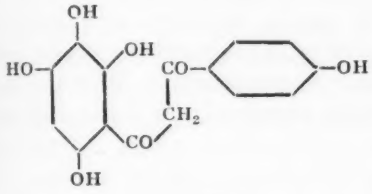
The phenomenon of ring isomerisation in flavones and related compounds was discussed in detail in a recent paper by Mukerjee, Seshadri and Varadarajan.[5] While flavones undergo ready isomeric change in the presence of boiling hydriodic acid, flavonols do not. The possibility of a similar isomeric change in the flavone type of anthocyanidins (*e.g.*, carajuridin)



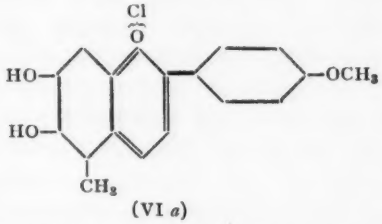
IV



V *a*, R=H
V *b*, R=CH_3



VI



(VI *a*)

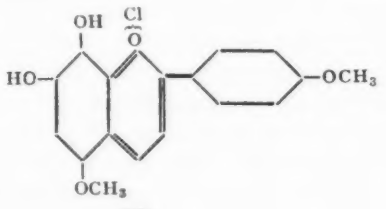
has not so far been investigated. Based on the analogy with flavones mentioned above, carajuridin chloride could be considered to have the alternative constitution of 5:4′-dimethoxy-7:8-dihydroxy flavylium chloride (VII) undergoing isomeric change during demethylation to yield carajuretin chloride. Evidence against this constitution was supplied in part in our previous communication[1] in which we pointed out the marked difference in the colour reactions exhibited by 6:7 and 7:8-dihydroxy flavylium salts. 6:7-Dihydroxy-4′-methoxy flavylium chloride exhibited reactions very similar to those of carajuridin whereas 7:8-dihydroxy-4′-methoxy flavylium chloride was very different. As a more appropriate example of 6:7-dihydroxy type of flavylium salts, 5-methyl-6:7-dihydroxy-4′-methoxy flavylium chloride (VI *a*) has now been prepared by the condensation of 2:4:5-trihydroxy-6-methyl benzaldehyde with *p*-methoxy acetophenone. This product also exhibits properties very similar to carajuridin. Obviously a methoxyl, a methyl group and a hydrogen atom in the 5 position are equivalent as far as colour reactions are concerned. Although on the basis of these observations, we could eliminate the possibility of carajuridin having the alternative structure (VII) no conclusive proof was provided for the view that 5:4′-dimethoxy-7:8-dihydroxy flavylium chloride could not undergo isomeric change on demethylation.

This question has now been settled by studying the demethylation of the closely related compound, 5:8:4′-trimethoxy-7-hydroxy flavylium chloride (VIII), with hydriodic acid. The compound (VIII) has now been prepared by condensing 2:4-dihydroxy-3:6-dimethoxy benzaldehyde with *p*-methoxy

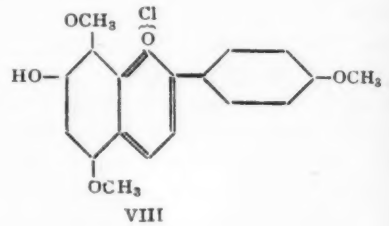
acetophenone. The product has been demethylated with hydriodic acid in the usual way. The resulting flavylium iodide (IX) has been isolated and its colour reactions recorded. It has been converted into the corresponding colour-base and finally into the flavylium chloride according to the method adopted by Pratt and Robinson.[6] The colour-base as well as its hydrochloride are markedly different from carajuretin and carajuretin hydrochloride respectively (*see* table); in ferric chloride colour and colour of solutions they are very similar to 7:8-dihydroxy-4′-methoxy flavylium chloride and its colour-base. The product of demethylation of 5:8:4′-trimethoxy-7-hydroxy flavylium chloride should therefore by 5:7:8:4′-tetrahydroxy flavylium chloride (XI), an isomer of carajuretin hydrochloride; the colour-base (X) has been given the name ' isocarajuretin '. The properties of carajuretin and isocarajuretin have been compared and the results are embodied in the table given below:—

TABLE

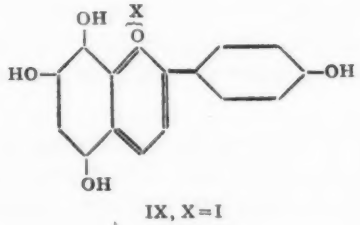
	Carajuretin (Chapman, Perkin and Robinson)	Isocarajuretin (Present work)
1 Heating ··	Turns black and decomposes at about 330°; does not have any melting point	Melts with decomposition at 239–40°
2 Colour of solutions ··	Gives red solution in alcohol	Gives purple coloured solutions in alcohol and ethyl acetate
3 Ferric-reaction ··	Deep purple	Brilliant emerald green



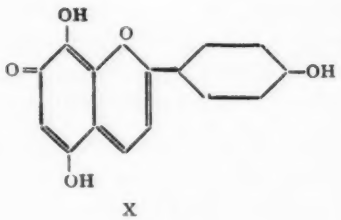
VII



VIII



IX, X=I
XI, X=Cl



X

The above experiments lead to the conclusion that the heterocyclic ring of the anthocyanidin molecule does not open under the influence of boiling hydriodic acid and confirm the constitution of Carajurin given by Chapman, Perkin and Robinson.

Experimental

5-Methyl-6: 7-dihydroxy-4'-methoxy flavylium chloride (*VI* a)

2: 4: 5-Trihydroxy-6-methyl benzaldehyde (0·5 g.) the preparation of which by the nuclear oxidation of orcylaldehyde will be described elsewhere,[8] and *p*-methoxy acetophenone (0·9 g.) were dissolved in glacial acetic acid (30 c.c.) and the solution saturated with dry hydrogen chloride at 25°. After standing for 2 days, the precipitated flavylium chloride (0·45 g.) was filtered off and washed with ether thoroughly and crystallised from hydrochloric acid (10%). Excess of ether was added to the remaining acetic acid solution when a further quantity (0·5 g.) was precipitated. The crystallised flavylium chloride formed glistening orange red needles which melted with decomposition at 223–24° (Found: C, 56·9; H, 5·3. $C_{17}H_{15}O_4$ Cl, $2H_2O$ requires C, 57·5; H, 5·4%). It gives a dull violet colour with aqueous sodium carbonate and forms a brownish orange solution in aqueous sodium hydroxide. Its orange red amyl alcoholic solution becomes deep red on the addition of sodium acetate and a drop of ferric chloride changes the red to deep purple. It leaves a red stain on the skin; is stable in the oxidation test and is almost completely extracted by the cyanidin reagent.

5: 8: 4'-Trimethoxy-7-hydroxy flavylium chloride (*VIII*)

2: 4-Dihydroxy-3: 6-dimethoxy benzaldehyde[7] (3·0 g.) and *p*-methoxy acetophenone (4·5 g.) were dissolved in glacial acetic acid (100 c.c.) and saturated with dry hydrogen chloride at room temperature (25°). The reaction mixture was allowed to stand for 2 days, when a portion of the flavylium chloride formed, crystallised out. It was filtered off and the remainder obtained from the acetic acid solution by precipitation with ether. It was crystallised from 10% alcoholic hydrochloric acid when small aggregates of needles were obtained (Found: C, 57·3; H, 4·9. $C_{18}H_{17}O_5$ Cl, 1·5 H_2O requires C, 57·5; H, 5·3%). It formed a deep red solution in aqueous sodium carbonate, a crimson red solution in aqueous sodium hydroxide and gave no colour with ferric chloride. Extraction by cyanidin reagent was fairly high.

5: 7: 8: 4'-Tetrahydroxy flavylium iodide (*IX*)

5: 8: 4'-Trimethoxy-7-hydroxy flavylium chloride (2·5 g.) was mixed with phenol (12·5 g.) and hydriodic acid (90 c.c., *d*, 1·7) and heated by

means of a glycerol bath in an atmosphere of carbon dioxide for 2 hours. After the evolution of methyl iodide had completely stopped, the reaction vessel was removed from the glycerol bath, cooled and a little water (25 c.c.) and much ether (75 c.c.) were added to the reaction mixture and left in the refrigerator for a day. A deep red (almost black) microcrystalline solid separated out. The flavylium iodide (2·4 g.) thus obtained was filtered and washed thoroughly with ether. It gave a deep red solution in amyl alcohol, which became violet on the addition of solid sodium acetate. A drop of ferric chloride changed the violet to a brilliant green.

Isocarajuretin (*X*)

The above flavylium iodide (2 g.) was ground well with aqueous sodium acetate and then filtered. The colour-base (1·5 g.) thus obtained, was crystallised from ethyl acetate when glistening brownish purple rectangular plates were obtained (Found: C, 67·1; H, 4·2. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). It melted with decomposition at 239–40°, was sparingly soluble in alcohol and ether, dissolved in amyl alcohol forming a deep purple solution, gave a rich green colour with ferric chloride in alcohol and did not stain the skin.

Isocarajuretin hydrochloride (*XI*)

Isocarajuretin (0·2 g.) was boiled with 3% aqueous hydrochloric acid (15 c.c.) for 15 minutes and then cooled. The solid was filtered off and crystallised twice from alcoholic hydrochloric acid (5%) when purplish red short stout rectangular prisms (0·1 g.) melting with decomposition at 239–40° were obtained (Found: C, 59·1; H, 4·1. $C_{15}H_{11}O_5Cl$ requires C, 58·7; H, 3·6%). Like the colour-base, it dissolved sparingly in aqueous sodium carbonate giving a brownish red colour and formed a deep green solution in aqueous sodium hydroxide which became brownish yellow on standing. Its extractability by the cyanidin reagent was poor.

SUMMARY

7-Hydroxy-5:8:4′-trimethoxy flavylium chloride has now been prepared and subjected to demethylation with hydriodic acid. The resulting flavylium iodide and the colour-base (Isocarajuretin) and the flavylium chloride obtained from it, are different from carajuretin and its salts. Hence it is concluded that no isomeric change takes place during the demethylation of derivatives of 5:7:8-hydroxy-flavylium salts related to flavones, supporting the constitution of carajurin, given by Chapman, Perkin and Robinson.

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NUCLEAR REDUCTION IN THE 5-POSITION OF ANTHOXANTHINS

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Received September 15, 1953

In continuation of our earlier publication,[1] the nuclear reduction of the 5-hydroxyl group in anthoxanthins is considered in this paper. There are actually more compounds without this hydroxyl group than without the 7-hydroxyl group. The following are the most important among flavones and flavonols: pratol (7-hydroxy 4′-methoxy flavone), fisetin (3:7:3′:4′-tetrahydroxy flavone), auranetin (3:6:7:8:4′-pentamethoxy flavone), robinetin (3:7:3′:4′:5′-pentahydroxy flavone), kanugin (3:3′:7-trimethoxy-4′:5′-methylenedioxy flavone), karanjin (3-methoxy-7:8-furano flavone). It was suggested previously by Seshadri and co-workers[2] that these compounds should arise from more fundamental 5:7-dihydroxy compounds by a process of reduction in the 5-position taking place at some stage of their evolution. In the case of auranetin it appeared that this happened to be the last stage.[3] In support of this theory as model laboratory experiments, the conversion of chrysin, apigenin, galangin and quercetin into the corresponding 5-desoxy compounds has been carried out. They are first methylated to produce their partial methyl ethers having only the 5-hydroxyl free. These readily form their tosyl derivatives which undergo smooth reduction with hydrogen in the presence of Raney nickel catalyst at room temperature to yield the 5-desoxy compounds (7-methoxy-, 3:7-dimethoxy-, 7:4′-dimethoxy- and 3:7:3′:4′-tetramethoxy flavones). The immediate product of reduction is in each case a mixture containing the unchanged compound, but the separation can be easily effected by following the two methods which are given in detail in the experimental part.

Experimental

Chrysin, apigenin, galangin and quercetin were subjected to partial methylation using the required quantity of dimethyl sulphate and excess of anhydrous potassium carbonate in acetone solution.[4]

Tosylation

A solution of each of the above partial methyl ethers (5-hydroxy flavones) (0·01 mole) in dry acetone was refluxed with toluene-*p*-sulphonyl chloride

(0·03 mole; excess) and ignited potassium carbonate (20–25 g.) on a water-bath until the product gave no colour with alcoholic ferric chloride (15 hours). Acetone was then removed and the residue was treated with cold aqueous potash (5%, 100 c.c.), when the tosyl esters separated as a fine powder. They were filtered, washed with water and a few c.c. of warm alcohol and then crystallised from the same solvent. Yield, nearly quantitative. The particulars of these tosyl esters are given below: 5-Tosyloxy tecto-chrysin separated in the form of colourless rhombic tablets melting at 207–8° (Found: C, 65·4; H, 4·2; $C_{23}H_{18}SO_6$ requires C, 65·4; H, 4·2%). 5-Tosyloxy apigenin dimethyl ether formed colourless prismatic needles melting at 185–86° (Found: C, 63·8; H, 4·6; $C_{24}H_{20}SO_7$ requires C, 63·7; H, 4·4%). 5-Tosyloxy-galangin dimethyl ether came out as colourless rectangular plates melting at 164–65° (Found: C, 64·0; H, 4·6; $C_{24}H_{20}SO_7$ requires C, 63·7; H, 4·4%). 5-Tosyloxy-quercetin tetramethyl ether crystallised as colourless small prismatic needles melting at 146–47° (Found: C, 58·8; H, 5·1; $C_{26}H_{24}SO_9$, H_2O requires C, 58·8; H, 4·9%).

Raney nickel Reduction

The tosyl ester (1 g.) was dissolved in alcohol (300–400 c.c.) and Raney nickel, prepared according to the method of Mozingo,[5] (3 teaspoon-ful) added. A stream of purified hydrogen gas was passed for 1 hour through this mixture which was shaken vigorously all the time. The solution was decanted off; the nickel residue decomposed with dilute hydrochloric acid and the resulting mixture extracted with ether (Ether solution E). The alcoholic solution was concentrated to 25 c.c. under diminished pressure and the concentrate was mixed with the residue left after evaporating off the ether solution (E). This alcoholic solution was then refluxed with aqueous potash (1·5 g. in 1 c.c.) for 40 minutes; alcohol was removed in vacuum and the resulting mixture (M) treated in two ways:

(i) Aqueous sodium hydroxide (5%, 50 c.c.) was added and the whole mixture extracted with ether. The ether solution, after being dried over anhydrous sodium sulphate, was concentrated and the residue was crystallised as given below.

(ii) The mixture (M) was acidified and the solid product filtered, washed with water and dried. It was dissolved in absolute alcohol and exactly 1 mole of alcoholic sodium hydroxide (calculated on the tosyl ester taken) was added to it. Alcohol was removed on a water-bath as quickly as possible and the residue left was extracted with benzene leaving behind the sodium salt of the unchanged 5-hydroxy flavones. The benzene solution on evaporation gave the desoxy compounds which could be crystallised as follows.

7-Methoxy flavone

It crystallised from ethyl acetate-petroleum ether and melted at 110°, undepressed with an authentic sample obtained by methylation of 7-hydroxy flavone with dimethyl sulphate using the potassium carbonate-acetone method. Robinson and Turner[6] also reported its m.p. as 110°. It exhibits blue fluorescence in concentrated sulphuric acid.

Pratol-methyl ether (7 : 4′-Dimethoxy flavone)

When crystallised from methyl alcohol it came out as colourless needles melting at 143–44° as reported by Tambor.[7] It also dissolves in concentrated sulphuric acid to give a yellow solution showing blue fluorescence.

3 : 7-*Dimethoxy flavone*

It crystallised from methyl alcohol as colourless rectangular prisms melting at 125–6° alone or when mixed with an authentic sample prepared from synthetic 7-hydroxy-3-methoxy flavone by dry methylation with dimethyl sulphate.

Fisetin tetramethyl ether (3 : 7 : 3′ : 4′-Tetramethoxy flavone)

It was obtained as colourless needles (m.p. 149–50°) when crystallised from ethyl acetate-petroleum ether and recrystallised from ethyl acetate (Allan and Robinson[8] reported the melting point as 150°). The melting point was considerably depressed when mixed with quercetin 3 : 7 : 3′ : 4′-tetramethyl ether, and moreover the product did not give any ferric reaction.

SUMMARY

Partial methyl ethers of chrysin, apigenin, galangin and quercetin have been subjected to nuclear reduction in the 5-position through their tosyloxy compounds. The products are 7-methoxy flavone, pratol methyl ether, 3 : 7-dimethoxy flavone and fisetin tetramethyl ether respectively.

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THE EFFECT OF SUBSTITUTION ON THE LIGHT ABSORPTION OF NAPHTHALENE

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Received June 3, 1953

A survey of the available data on the absorption spectra of monosubstituted naphthalene derivatives indicates that, irrespective of the nature of the substituent group, β-substitution results in a larger bathochromic shift than α-substitution, the only exception being the phenylnaphthalenes (Table I). Hirshberg and Jones have divided the spectrum of naphthalene into three distinct regions of absorption (A, B and C bands).[1] Unlike the case of anthracene, assignments of the absorption regions of naphthalene to polarization in definite directions have not been made conclusively.[2] However, working on a single naphthalene crystal, Matsen has recently assigned the longest wavelength band in naphthalene to polarization along the long axis of the molecule.[3]

Table I

*Longest wavelength band of naphthalene derivatives**

Substituent group	λ in mμ	
	α	β
Phenyl (–Ph) ..	*Ca* 288	288
Carboxyl (–COOH) ..	*Ca* 293	*Ca* 336
Methyl ($-CH_3$) ..	*Ca* 316	319
Amino ($-NH_2$) ..	322	340
Nitro ($-NO_2$) ..	323	356
Hydroxyl (–OH) ..	*Ca* 324	*Ca* 334

* The data are collected from literature.

Hirshberg and Jones[1] conclude from the nature of the absorption curves of α- and β-substituted naphthalene derivatives that in the α-derivatives "the B and C groups of bands become fused into a single band, probably as a result of broadening and bathochromic displacement of the B band

group (the middle band group) and its superposition on the weaker longest wavelength C band group, whereas in the β-substituted derivatives, the B band group does not move at all, and the C band group is displaced bathochromically and greatly intensified." They have also suggested that the B and C band groups may be due to electronic excitation along the short and long axis of the molecule respectively.

The experiments now reported throw further light on the nature of the changes that take place in the naphthalene spectrum on substitution. It is assumed that, when alcoholic solutions of α- and β-substituted naphthalene derivatives are evaporated in an electrical field, the molecules deposited will orient themselves in such a way that the electrical axis of the molecule is in line with the direction of the applied field. Examination of the spectra obtained by passing light through a thin film of oriented molecules of substituted naphthalene derivatives shows that for both the α- and β-substituted derivatives the longest wavelength band is polarized perpendicular to the electrical axis of the molecule. The resultant dipole moment of both α- and β-substituted naphthalene derivatives will have components, whose magnitude will change with the nature and position of the substituent group, along the short and long axis of the molecule. The α-substituted derivatives have a major dipole component along the short axis of the molecule, and the β-substituted derivatives along the long axis of the molecule. The two substituted naphthalene derivatives will hence be oriented approximately in mutually perpendicular directions. Therefore, the absorption corresponding to the longest wavelength band of α- and β-substituted naphthalene derivatives is due to electronic excitation in directions perpendicular to each other and it is clear that the long wavelength absorption is due to excitation along the short axis of the α-substituted molecules and to excitation along the long axis of the β-substituted molecules. Moreover, the results provide at least qualitative evidence that when substitution at the β-position of naphthalene takes place the longest wavelength band is the C band of naphthalene which has undergone a bathochromic shift, and that in the α-derivatives it is the B band which is principally displaced and is superimposed on the weak C band of naphthalene; and this also explains why the longest wavelength band is at a longer wavelength in the β-substituted naphthalene derivatives than in the corresponding α-isomers.

The effect of disubstitution on the spectrum of naphthalene is much more complicated, and several factors have to be considered. From the fact that β-substitution produces a greater bathochromic shift of the naphthalene spectrum than α-substitution, it can be assumed that β: β-disubstitution

should produce a larger bathochromic shift than α: α- or α: β-disubstitution. Three β: β-disubstituted isomers are possible: the 2: 3-, the 2: 6- and 2: 7-derivatives. Since the 2- and 7-positions of naphthalene are not conjugated, it may be anticipated that 2: 3- and 2: 6-disubstitution will produce the maximum bathochromic shift of the naphthalene spectrum. Whether the 2: 3- or the 2: 6-disubstitution will give the maximum shift will depend on three main considerations: (1) the possibility of chelation in the 2: 3-disubstituted derivatives; (2) the nature of the substituent groups involving three further possibilities: (*a*) both the substituent groups are *o*, *p*-directing; (*b*) both are *m*-directing; and (*c*) one is *o*-,*p*-directing and the other *m*-directing; (3) the possibility and extent of steric hindrance of the substituents in the 2: 3-positions. The available data for the disubstituted naphthalene derivatives are inadequate for any generalization regarding the relative bathochromic effect of substitution in the 2: 3- and 2: 6-positions.

Fig. 1 shows the absorption spectra of four isomeric hydroxynaphthoic acids: 1-hydroxy-2-naphthoic acid, 2-hydroxy-1-naphthoic acid, 2-hydroxy-

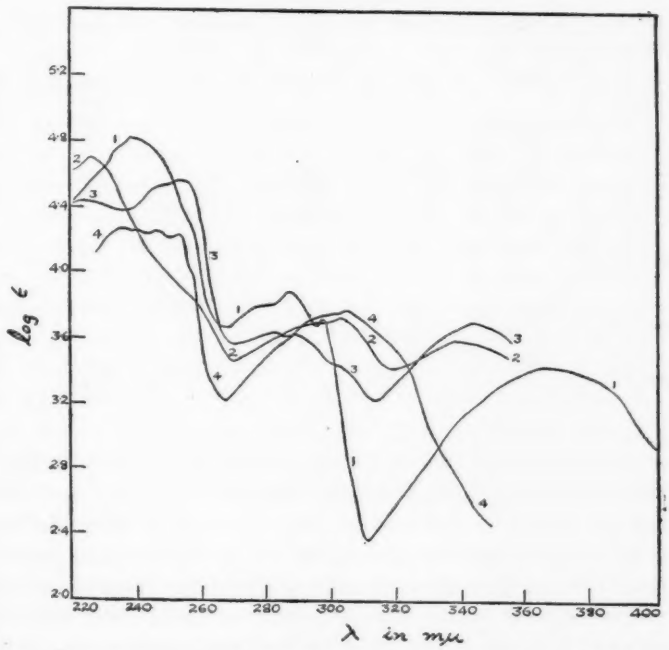


FIG. 1. Absorption spectra of (1) 2-hydroxy-3-naphthoic acid; (2) 2-hydroxy-1-naphthoic acid; (3) 1-hydroxy-2-naphthoic acid; and (4) 2-hydroxy-6-naphthoic acid in dioxane.

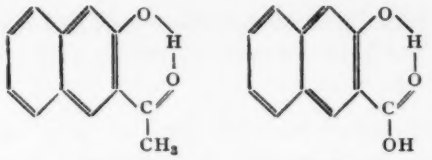
3-naphthoic acid and 2-hydroxy-6-naphthoic acid; Table II gives the values of the absorption maxima and intensities. The β: β-disubstituted 2-hydroxy-3-naphthoic acid has its longest wavelength absorption maximum at a wavelength higher than the other three acids. However, the other β: β-disubstituted derivative, 2-hydroxy-6-naphthoic acid, has its longest wavelength absorption maximum at a lower wavelength than the 2: 1-isomer. This is perhaps due to chelation between the adjacent substituents in the 2: 1-isomer.

TABLE II

The wavelengths and intensities of absorption maxima of certain disubstituted naphthalene derivatives

Compound	λ max	log ε	λ max	log ε	λ max	log ε
	in mμ		in mμ		in mμ	
2-Hydroxy-3-naphthoic acid	366	3·45	297 286 276	3·73 3·89 3·78	239	4·81
2-Hydroxy-1-naphthoic acid	337	3·60	304 294	3·73 3·69	226	4·68
2-Hydroxy-6-naphthoic acid	304	3·77	..	..	253 246 240 236	4·24 4·26 4·25 4·26
1-Hydroxy-2-naphthoic acid	342	3·71	301·5 289 279	3·47 3·62 3·64	254 222	4·56 4·42
2-Methoxy-3-naphthoic acid	341	3·25	279 270	3·73 3·74	234	4·71
2-Methoxy-1-naphthoic acid	333 322·5	3·45 3·41	280	3·77	230	4·80
2-Methoxy-6-naphthoic acid	299	4·01	..	..	252 244 238	4·59 4·66 4·68

Baker and Caruthers[4] observed that, among the isomeric acetyl naphthols, 3-acetyl-2-naphthol is bright yellow, whereas the isomers are colourless. It was suggested earlier by Baker *et al.*[5] that chelation between the hydroxyl and acetyl groups depends on the presence of a double bond between the carbon atoms bearing these groups; they assigned the chelated structure (I) to 3-acetyl-2-naphthol in which the C_2-C_3 bond of naphthalene was " fixed " as a double bond and one of the benzene rings was *o*-quinonoid. However, since 3-acetyl-2-naphthol shows none of the properties of a true *o*-quinonoid



(I) (II)

compound they concluded that the " colour is due to some disturbance of the normal naphthalene structure set up by the process of chelation". Bergmann and Berlin[6] ascribed the formation of a copper complex by the oxime of 3-acetyl-2-naphthol to the presence of a double bond in the C_2-C_3 positions of naphthalene.

Recently, Bergmann *et al.*[7] have drawn attention to the fact that, whereas 2-hydroxy-3-naphthoic acid and its methyl ester are coloured yellow, 2-methoxy-3-naphthoic acid and 2-hydroxy-1- and 1-hydroxy-2-naphthoic acids are colourless compounds. Following Baker, they associate the colour of the 2:3-acid with enhanced double bond character of the bond between the C_2-C_3 atoms of naphthalene, as a result of chelation between the 2- and 3-substituents and consequent formation of an *o*-quinonoid ring system. They assigned to the 2:3-acid a structure (II) corresponding to Baker's structure for 3-acetyl-2-naphthol.

A little earlier Melchoir[8] determined the absorption spectra of isomeric *o*-hydroxynaphthaldehydes and their negative ions. He accounted for the deeper colour of the 2:3-isomer by a theory involving the choice of arbitary polar structures for the resonance possibilities in the ground and excited states, based on two considerations; one was, as others had shown earlier, that the 2:3-bond in naphthalene has less double bond character than the 1:2-bond and therefore that the chelation in 2-hydroxy-3-naphthaldehyde is weaker; the other was an assumption made by him that the longest wavelength band arises from the carbonyl group. He expected that the 2:3-isomer had the highest energy both in the ground and excited states, but that the energy difference between the upper and lower states of the 2:3-compound was lower than the corresponding difference for the isomers; it therefore followed that the absorption maximum should appear at a lower frequency as observed.

Among the three isomeric *o*-hydroxynaphthoic acids (the 2:3-, 2:1- and 1:2-acids), hydrogen bonding between the hydroxyl and the carbonyl group must occur. Whether the relative strength of hydrogen bonding leads to the deeper colour of 2:3-hydroxynaphthoic acid is open to question. The explanation given so far has rested on two interdependent factors:

the strength of chelation between the substituents and the degree of double bond character of the bond between the carbon atoms to which the substituents are attached.

When the three hydroxynaphthoic acids or their esters are chromatographed on alumina, using benzene as solvent and eluant, the 2:1- and 1:2-acids and esters move down quicker than the 2:3-isomers. Since chelation in azophenols and aminoanthraquinones has been shown to play a vital role in the adsorption process,[9] the greater adsorbability of the 2:3-acid and ester as compared to the 2:1- and 1:2-isomers indicates the lower strength of the internal hydrogen bond in the 2:3-acid and ester. Hunsberger[10] has found by infra-red measurements that the strength of chelation in 1:2- and 2:1-disubstituted naphthalene derivatives is practically equal and considerably greater than the strength of chelation in the 2:3-isomer. In fact, in the case of the nitronaphthylamines Hathaway and Flett[11] have shown by infra-red measurements that weak or practically no hydrogen bonding exists in 2-nitro-3-naphthylamine, whereas in the 2:1- and 1:2-isomers there is evidence for hydrogen bond formation.

It is thus apparent that the observed differences in the strength of chelation of 1:2, 2:1 and 2:3-derivatives of naphthalene indicate the greater double bond character of the C_1-C_2 bond in comparison with the C_2-C_3 bond of naphthalene. Recently Coulson and others calculated the bond orders for various bonds in a large number of polycyclic compounds, and for naphthalene they obtained a bond order of 1·725 for the C_1-C_2 bond, whereas for the C_2-C_3 bond the value was 1·603. Any extranuclear effect due to chelated *o*-substituents must be the same for all the three isomers, and variations in the strength of chelation can only be due to differences in the double bond character of the C-C bond. Hunsberger points out that the converse effect of chelation enhancing the double bond character must be small, since such " induced " fixation cannot exceed the contribution of a structure with the included bond as double by more than 10% over the normal contribution.[10] Thus Bergmann's explanation that the deeper colour of the 2:3-disubstituted chelated naphthalene derivatives is due to the major contribution of the unsymmetrical naphthalene structure is not substantiated.

Since 2-methoxy-3-naphthoic acid is colourless and chelation is not possible in this compound, Bergmann *et al.* adduced the greater bathochromic shift in the spectrum of 2-hydroxy-3-naphthoic acid in comparison with its isomers as due to hydrogen bonding between the adjacent hydroxyl and carboxyl groups. However, a comparison of the spectra of 2-methoxy-3-naphthoic, 2-methoxy-1-naphthoic and 2-methoxy-6-naphthoic acids (Fig. 2)

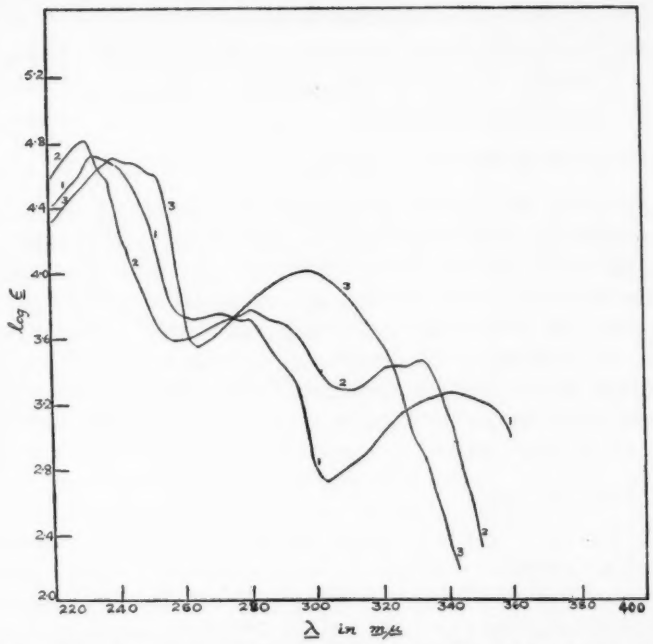


FIG. 2. Absorption spectra of (1) 2-methoxy-3-naphthoic acid; (2) 2-methoxy-1-naphthoic acid; and (3) 2-methoxy-6-naphthoic acid in dioxane.

shows that, even among the methoxynaphthoic acids, 2:3-disubstitution effects the largest bathochromic shift. The 2:1-derivative absorbs at a longer wavelength than the 2:6-isomer. The fact that 2-methoxy-3-naphthoic acid absorbs at a longer wavelength than the 2:1-isomer is understandable. Further, Hirshberg and Jones have shown that the steric effect of a carboxyl group in the 1-position on the *peri* hydrogen atom is increased considerably when there is another carboxyl group or other large substituent in the 2-position.[1] This perhaps accounts for the large bathochromic shift of the naphthalene spectrum in 2-methoxy-1-naphthoic acid in comparison with the 2:6-isomer.

It is thus seen that the order of the position of the longest wavelength band in the disubstituted naphthalenes can be explained principally on the basis of the α- and β-substitution, after taking into consideration the possibility of chelation and steric hindrance in the molecule. The effect of the nature of the substituent on the light absorption of disubstituted naphthalenes cannot be easily predicted, since much more extensive data than we have available at present are necessary.

EXPERIMENTAL

2-Hydroxy-3-naphthoic acid, 2-hydroxy-1-naphthoic acid and 1-hydroxy-2-naphthoic acid were commercial samples which were purified by chromatography and repeated crystallization.

2-Hydroxy-6-naphthoic acid

6-Bromo-2-naphthol[12] was methylated and converted to 6-cyano-2-methoxynaphthalene after Seligman and Rutenberg.[13] This nitrile (2 g.) was boiled with 10% aqueous caustic soda (100 c.c.) till it went completely into solution (3 hours). Acidification and crystallization of the precipitate from dilute alcohol gave colourless needles of 2-methoxy-6-naphthoic acid, m.p. 209°. Demethylation by means of hydrobromic acid[14] yielded 2-hydroxy-6-naphthoic acid, which crystallized from water in colourless needles, m.p. 245–48° (Knowles *et al.*[14] quote m.p. 245–48°; Butler and Royle,[15] 240–41°; and Cason,[16] 243–44°).

2-Methoxy-3-naphthoic acid

2-Hydroxy-3-naphthoic acid (2 g.) was dissolved in 20% caustic soda solution (150 c.c.) and freshly distilled dimethyl sulphate (15 c.c.) was added slowly during 30 minutes. The mixture was warmed on a water-bath at 60–70° till the product gave no colouration with ferric chloride. The mixture was then boiled for 4 hours to hydrolyse the ester. 2-Methoxy-3-naphthoic acid crystallized from dilute alcohol in colourless needles, m.p. 134–35° (Cohen *et al.*, 134–35°).[17]

2-Methoxy-1-naphthoic acid

This was prepared as above from 2-hydroxy-1-naphthoic acid and this crystallized in prisms from dilute alcohol, m.p. 176° (decomp.) (Rousset,[18] 176°).

The methyl esters of 2-hydroxy-3-naphthoic, 2-hydroxy-1-naphthoic and 1-hydroxy-2-naphthoic acids were prepared in the usual manner by boiling the acids in methyl alcohol in presence of a little concentrated sulphuric acid.

Chromatography of hydroxynaphthoic acids

A benzene solution (10 c.c.) of a mixture of 2-hydroxy-3-naphthoic, 2-hydroxy-1-naphthoic and 1-hydroxy-2-naphthoic acids was passed through a column of alumina (10×1·5 cm.) and developed with benzene (150 c.c.). On examining the column in ultraviolet light two zones were observed: a greenish-yellow fluorescent zone of 2-hydroxy-3-naphthoic acid at the top

and a bluish fluorescent zone of 2-hydroxy-1-naphthoic and 1-hydroxy-2-naphthoic acids in the middle of the column; the latter two acids did not separate under these conditions.

The chromatographic separation of the esters of the above three acids was similarly observed.

Absorption of polarized light by naphthalene derivatives

A 1% alcoholic solution of the naphthalene derivative (5 c.c.) was evaporated in a small petri dish in which was placed a silica plate. The solution under evaporation was submitted to the influence of an electrical field by placing the dish between two copper rods which were connected to the two leads of a transformer giving a field above 2,000 volts. After complete evaporation, the silica plate, now coated with a thin layer of the oriented molecules of the compound under investigation, was immediately placed in front of the slit of a Hilger medium quartz spectrograph in such a way that the edge of the plate parallel to the field was parallel to the slit of the spectrograph. Light from a stabilized hydrogen lamp was polarized by means of a nicol and passed through the coated silica plate. The spectrum was recorded on a Kodak process plate and for every derivative studied two adjacent spectra were obtained using a Hartmann diaphragm, one with the light polarized parallel to the direction of the electrostatic field and the other perpendicular. The intensities of the absorption of light polarized in the two directions were compared qualitatively in the corresponding regions of absorption.

The following naphthalene derivatives were examined: (1) α-naphthol; (2) β-naphthol; (3) α-naphthylamine; (4) β-naphthylamine; (5) α-nitronaphthalene; and (6) β-nitronaphthalene.

Absorption spectra

The absorption spectra of the various compounds recorded were determined on a calibrated Beckmann Model DUV spectrophotometer, using dioxane as solvent. The concentration of the solution was so chosen as to give the density readings within the range 0·3–0·8, using in all cases a 1 cm. cell. More than one concentration had to be used for some compounds in order to record the complete spectrum.

SUMMARY

A qualitative method for assigning the longest wavelength band in the absorption spectra of α- and β-monosubstituted naphthalene derivative

to polarizations in definite directions has been devised. The longest wavelength band in the absorption spectra of α-substituted derivatives is shown to be due to polarization along the short axis of the molecule; in the spectra of the β-substituted derivatives the longest wavelength band is due to polarization along the long axis of the molecule. The absorption spectra of four isomeric hydroxynaphthoic acids have been determined, using dioxane as solvent. The deeper colour of 2:3-hydroxynaphthoic acid in comparison with the isomeric acids is explained as due to β:β-disubstitution in the naphthalene nucleus. The absorption spectra of 2-methoxy-1-naphthoic acid, 2-methoxy-3-naphthoic acid and 2-methoxy-6-naphthoic acid are discussed.

ACKNOWLEDGMENT

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ANTHRAQUINONE AND ANTHRONE SERIES

Part XI. Steric Hindrance in Dibenzanthronyls and Dibenzanthrones

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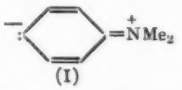
Many examples are available concerning the effects of steric hindrance to the planarity of organic molecules on their absorption spectra. A common influence of such steric hindrance is a reduction in the intensity of maximum absorption, usually but not invariably accompanied by a hypsochromic shift in the long wavelength absorption. Changes in the absorption spectra as a result of steric hindrance to planarity can be related to its interference with the resonance of the molecule either in the ground or excited states. Steric hindrance in the excited state decreases the resonance stabilization of that state and increases the transition energy, leading therefore to a hypsochromic shift in the absorption spectrum. On the other hand, steric hindrance in the ground state decreases the energy of transition because of the reduced resonance stabilization of the ground state, and the consequence is a bathochromic shift in the absorption spectrum. Brooker *et al.*, while studying the effects of steric hindrance to planarity of dye molecules, have discussed two distinct types of behaviour. In the great majority of cases the compounds studied are characterized by a single low energy resonance structure. As a rule the crowding substituent does not affect this single dominant structure, which is usually benzenoid contributing principally to the ground state, but affects other higher energy structures, which contribute mostly to the excited states of the molecule, resulting in a hypsochromic shift of the spectrum. But in cases where the molecule can be represented by two identical structures of low energy, the effect of steric hindrance will be to decrease the contribution of these identical structures to the ground state of the molecule, thereby leading to a bathochromic shift.[1]

The effect of steric hindrance to the planarity of an aromatic ring system may be of varied character. In the simplest *o*-disubstituted benzene derivatives, the benzene nucleus, due to its high energy of resonance stabilization, will remain planar and the substituent groups will twist about the connecting bond to attain a state of least strain within the molecule. This destruction of the planarity of the whole molecule because of steric strain between the *ortho* substituents has been mentioned by Remick as one of the factors that contribute to the *ortho* effect in *o*-disubstituted aromatic ring systems.[2] O'Shaughnessy and Rodebush have determined the absorption spectra

of acetophenone and a few methyl substituted acetophenones and conclude that, when two methyl groups are in the $o:o'$-positions, coplanarity of the molecule is not possible because of steric hindrance between the adjacent methyl groups, leading to a striking decrease in absorption, at least at longer wavelengths.[3]

Remington[4] has studied the effects of steric hindrance on the absorption spectrum of dimethylaniline. He has suggested that any substituent group in the 2- or 6-position of dimethylaniline tends to oppose the coplanar configuration of the resonance structure (I), which he assumes to contribute

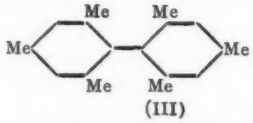


(I)

most to the excited state of the molecule. This nonplanarity increases the energy of the excited state more than that of the ground state, leading to absorption at higher frequencies. Further, the probability of the molecule to assume a strained planar form decreases, leading to a decrease in the absorption intensity. Working on similar dimethylaniline derivatives, Platt and Klevens have suggested that the loss of planarity by a "crowding" substituent causes the C = N linkage to twist and that the changes in the spectrum are quantitatively related to the angle of twist.[5]

The effect of steric factors on the absorption spectra of diphenyl derivatives has been thoroughly investigated.[3 6–12] The effect of substitution at the $o:o'$-positions in diphenyl is to twist the molecule around the C—C bond connecting the two benzene rings, in contrast to the twisting around the bond connecting the substituent group to the benzene ring in the case of the *o*-disubstituted benzene derivatives. The absorption of diphenyl is attributed to contributions made by structures such as (II), principally to the excited state of the molecule. Since this involves a double bond character for the C—C bond connecting the two phenyl residues, a planar configuration is necessary for the resonance to be effective. It follows from quantum mechanical considerations that the maximum amount of interaction is possible when the π orbitals are exactly parallel to each other and perpendicular to

(II)



(III)

the plane of the ring. If the overlap of the van der Waals radii of the $o:o'$-substituents is large, the molecule is twisted out of planarity with a resultant decrease in the contribution made by structures such as (II); the absorption

will then correspond roughly to that of two molecules of the corresponding benzene derivatives. Thus when the two benzene rings are forced into different planes as in dimesityl (III), the absorption corresponds to that of mesitylene ($\epsilon \times 2$) and not to that of a diphenyl derivative.

In the disazo dyes derived from benzidine increased insulation at the 1:1′-(diphenyl) bond appears when non-coplanarity is induced by substitution of methyl groups in the 2:2′- and 2:2′:6:6′-positions.[13] The non-linearity of the 2:2′-dihydroxybenzalazine molecule results in a splitting of the main absorption band of the 4:4′-isomer into two bands, one of shorter and the other of longer wavelength.[14]

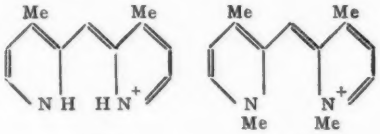
Friedel *et al.* have discussed the effects of steric hindrance on the spectra of the three dinaphthyls, on 1- and 2-phenylnaphthalene, and on diphenyl derivatives. They detected short wavelength peaks in the 205–12 *mμ* region for compounds containing two aromatic ring systems conjugated without steric hindrance; these bands and the longer wavelength bands appeared to converge towards each other when the coplanarity of the system was hindered by interfering groups. Because of the effect of steric hindrance the spectrum of 1:1′-dinaphthyl was very similar to that of naphthalene, except for the relative absence of fine structure; the spectrum of 2:2′ dinaphthyl clearly indicated conjugation and freedom from steric hindrance; 1:2′-dinaphthyl gave an intermediate spectrum. Comparing the spectra of 2-methyl-, 2-methoxy- and 2-hydroxydiphenyl, they found that steric hindrance was in the given decreasing order, as indicated by the hypsochromic shift in the 284 *mμ* band of diphenyl; however, the difference between the curves for 2-methoxy- and 2-hydroxydiphenyl was small, and the intensity of absorption in the 250–310 *mμ* region was less in the case of the phenol.[15]

Anthracene, 9-phenylanthracene and 9:10-diphenylanthracene have very similar spectra,[16] although the latter two compounds have one and two phenyl rings attached to the *meso* positions of the anthracene nucleus. The reason for this similarity is that the phenyl groups in the *meso* positions are not coplanar with the anthracene ring system because of steric hindrance; resonance as in diphenyl across the C—C bond connecting the anthracene and phenyl rings is therefore inhibited.

Smakula and Wassermann compared the absorption spectra of *cis*- and *trans*-stilbenes and observed that the *cis* isomer absorbs at a higher frequency and lower intensity than the *trans*.[17] The *trans* isomer has been proved to be planar,[18] while coplanarity is prevented in *cis*-stilbene by the interference of the *ortho* hydrogen atoms. Here again, as in the example of diphenyl, the effect of substituting a crowding group in the *ortho* positions of the two

phenyl residues is to twist the molecule around the bonds connecting the CH = CH group to the phenyl residues. As a result, the optically important resonance is weakened, decreasing light absorption.[19] A similar decrease in the absorption intensity and a slight decrease in the wavelength of maximum absorption have been found in *cis*-azobenzenes in comparison with the *trans* isomers.[20] While considering the stereochemistry of the carotenoids Zechmeister has drawn attention to the differences in the absorption of *cis* and *trans* isomers. "The hydrogen atoms of the =CH— groups adjacent to a double bond overlap somewhat in the *cis* configuration and the consequent interatomic repulsion tends to push the *cis* isomers out of planarity. This interference in conjugation shifts the spectral bands to shorter wavelengths."[21]

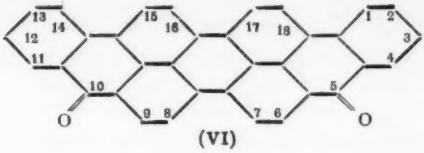
Brunings and Corwin have cited an example of steric hindrance to planarity in a dye molecule resulting in a shift of the longest absorption maximum to longer wavelength. The ion (IV) has λ max at 470 $m\mu$ and (V) at 510 $m\mu$; (IV) can be coplanar with a slight bending of the NH bonds, but the methyl groups in (V) preclude coplanarity of the two pyrrole rings. The effect of the crowding substituents is to twist the molecule around the bonds connecting the —CH= group to the two pyrrole residues. This departure from planarity raises the potential energy of (V) in the ground state so that the difference in the energies of the ground and excited



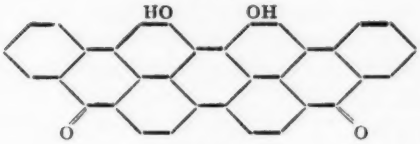
(IV) (V)

states becomes smaller and absorption occurs at longer wavelength.[22] Brooker *et al.*[1] have given a number of examples in which the crowding of the two nuclei of a cyanine out of a common plane leads to absorption at longer wavelength. These compounds belong to the class of molecules which have two identical low energy structures, the effect of steric hindrance to planarity being to increase the wavelength of maximum absorption.

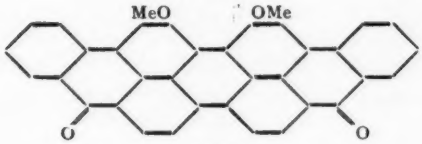
In all the cases so far reported, the effect of introducing two substituent groups in such positions as to make them sterically hinder each other is to twist the substituent group around the bond connecting the group to the parent nucleus, or to twist two parts of the molecule around a bridging linkage. In the present work the effect of introducing two crowding substituents in vicinal positions in a polynuclear aromatic ring system, which has an overriding tendency to remain planar, has been studied.



(VI)



(VII)



(VIII)

Fig. 1 shows the absorption spectra of dibenzanthrone (Violanthrone; VI) and three of its derivatives (16: 17-dihydroxy-, 16: 17- and 3: 12-di-

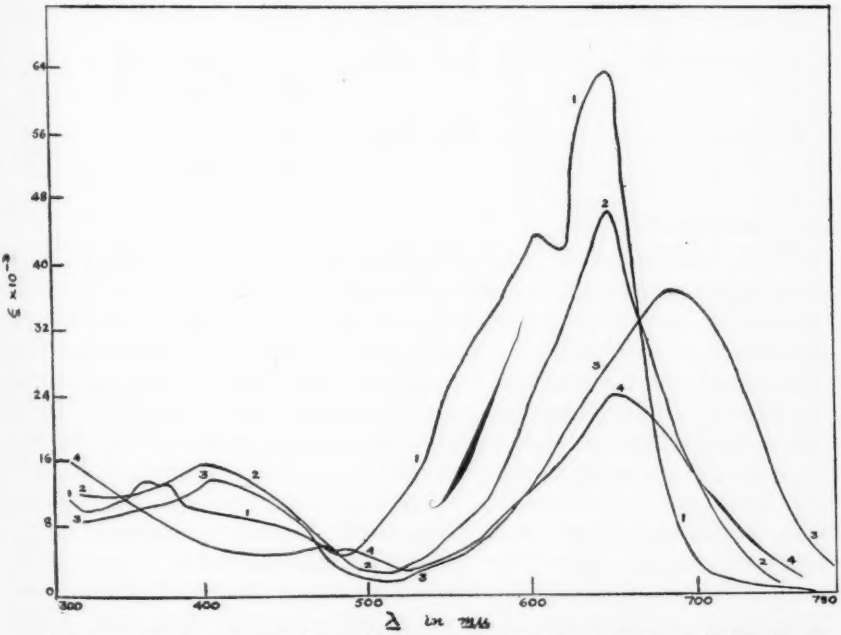


FIG. 1. Absorption spectra of (1) dibenzanthrone; (2) 16: 17-dihydroxy-dibenzanthrone; (3) 16:17 dimethoxydibenzanthrone; and (4) 3: 12-dimethoxydibenzanthrone in *o*-chlorophenol.

methoxydibenzanthrone; VII, VIII and IX) in *o*-chlorophenol; and Table I gives the wavelengths and intensities of the absorption maxima.

TABLE I

The Wavelengths and Intensities of Absorption Maxima of Dibenzanthrone and other Compounds

Compound	λ max in mμ	ε max	λ max in mμ	ε max	λ max in mμ	ε max
Dibenzanthrone ..	642 594	63,810 44,810	365 355	15,540 15,540	..	..
16 : 17-Dihydroxydibenzanthrone ..	647	47,600	395	16,000	..	..
16 : 17-Dimethoxydibenzanthrone ..	685	37,000	400	15,380	..	..
3 : 12-Dimethoxydibenzanthrone ..	650	23,160	472 462	28,800 28,800	..	..
Benzanthrone* ..	394	10,000	306 285 276	8,510 7,940 8,130	254 220	20,890 34,670
9-Methoxybenzanthrone ..	420 364 361 365·5	7,760 3,310 3,390 3,310	315	9,330	260 231	25,120 34,670
3 : 3′-Dibenzanthronyl ..	415	54,950	307 288 276	38,020 42,660 40,740	253 230 213	83,180 162,200 177,800
4 : 4′-Dibenzanthronyl ..	411	69,500	323 313 284	46,770 54,480 37,840	255 228 214	126,500 195,000 214,900

* Read from Ref. 27.

The spectrum of 16: 17-dihydroxydibenzanthrone shows a slight decrease in the intensity and a very insignificant increase in the wavelength of maximum absorption, whereas the 16: 17-dimethoxy compound exhibits a considerable decrease in intensity and a large bathochromic shift in comparison with the spectrum of dibenzanthrone. The bathochromic shift of the spectrum as we pass from dibenzanthrone to 16: 17-dimethoxydibenzanthrone may be due to two reasons. The first obvious reason is the introduction of the two auxochromic methoxyl groups; but the methoxyl groups can exercise their normal auxochromic effect only if they can enter into electronic interaction with the dibenzanthrone ring system, which in turn is contingent on the coplanarity of the methoxyl groups and the dibenzanthrone system. Since there is no pronounced shift of the spectrum on the introduction of two hydroxyl groups in the same 16: 17-positions, the shift in the spectrum of

the 16: 17-dimethoxy compound may be mainly due to the effect of steric hindrance of the vicinal methoxyl groups.

We have no data on the planarity of dibenzanthrone and its derivatives. However, the larger the number of benzene rings in a polynuclear aromatic ring system, the larger is the resonance stabilization energy of the molecule and one effect of this increased resonance will be an increased tendency for the ring system to retain coplanarity. It is therefore reasonable to assume that the dibenzanthrone molecule is planar. Disubstitution at the 16: 17-positions of dibenzanthrone will lead to steric interference between the two substituent groups. A scale drawing of the 16: 17-dimethoxydibenzanthrone molecule is given in Fig. 2, and the overlap of the van der Waals radii of the vicinal methoxyl groups is clear. If the molecule is constructed with

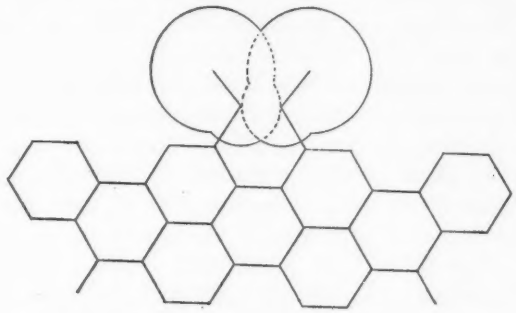


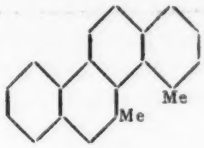
FIG. 2. Scale drawing of the 16: 17 dimethoxydibenzanthrone molecule.

Fisher-Hirschfelder-Taylor models, the interference is obvious, but as Jones has pointed out,[23] very great care has to be taken in making deductions from these models in border line cases.

One effect of steric hindrance between the two substituent methoxyl groups in the 16: 17-positions of dibenzanthrone can be to twist the methoxyl groups out of the plane of the aromatic ring system around the bonds connecting the substituent groups to the ring system. If this happened, the absorption spectrum of the dimethoxy compound must be similar to that of dibenzanthrone, because of the absence of resonance interaction between the ring system and the substituent groups. However, this is not true since the spectrum of the dimethoxy derivative is markedly different from that of the parent dibenzanthrone. A second possibility, that the methoxyl groups tend to twist the whole molecule out of planarity, is highly improbable as the high energy of resonance stabilization of the dibenzanthrone molecule will not allow such distortion. The most probable explanation seems to be

that, on account of the high energy of resonance stabilization, the polynuclear ring system of dibenzanthrone undergoes a slight adjustment of the bond angles and remains coplanar with the two methoxyl groups. Extra energy is needed to force the methoxyl groups into the same plane as the ring system in this manner. Westheimer and Mayer[12] have made theoretical calculations regarding the rate of racemization of sterically hindered (optically active) diphenyl derivatives. They assume, as suggested by Hill, that the energy of a strained molecule is distributed among many bonds and by no means concentrated in the energy of repulsion of the groups.[12] On this basis they calculate the activation energy of racemization which is the excess energy of the sterically hindered planar configuration over the nonhindered planar configuration. This excess energy, they show, depends upon the angle between the hindered substituent and the phenyl ring. However they find that the true activation energy can be found by substracting the resonance energy from the calculated energy of activation. Since it is assumed that the 16: 17-dimethoxydibenzanthrone molecule remains planar by adjustments in bond lengths and angles, the true activated complex state may be identified with the ground state, the ground state thus being raised from its normal level. The small decrease in the intensity, as well as a small increase in the wavelength of maximum absorption in the spectrum of 16: 17-dihydroxydibenzanthrone, as compared to the greater reduction in absorption intensity and a large bathochromic shift of the longest wavelength band of dimethoxydibenzanthrone, clearly indicates the more pronounced effects of steric hindrance in the dimethoxy compound in comparison with the dihydroxy analogue.

Among the spectra of the alkyl derivatives of various polycyclic aromatic hydrocarbons reported so far, it is only the data for the methylchrysenes that provide a similar example. Brode and Paterson[24] have shown that among the methylchrysenes the greatest bathochromic shift is found in the 4- and 5-methylchrysenes, although by analogy with 1: 2-benzanthracene the greatest bathochromic shift was predicted for 5- and 6-methylchrysenes,[25] and they suggest that this shift is due to steric hindrance between the methyl groups and the hydrogen atoms in the 4- and 5-positions and consequent distortion of the planar nature of the molecule. Such hindrance will be grately enhanced in 4: 5-dimethylchrysene (X), the absorption spectrum of which shows changes of greater magnitude.[25] From a scale drawing of the 4: 5-dimethylchrysene molecule, Newman has suggested three alternatives for the location of the methyl groups in such aromatic ring systems: (1) the methyl groups are coplanar with the ring system, but bent away from one another; (2) the aromatic rings are distorted; or (3) the ring

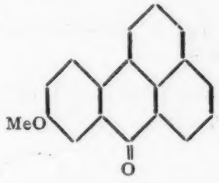


(X)

system and the methyl groups are not in the same plane. Newman considers the last as the most prabable explanation.[26] However, in the light of the present treatment of the absorption spectrum of dimethoxydibenzanthrone, it is suggested that the dimethylchrysene molecule as a whole, by adjustments in the bond lengths and angles, is coplanar, and since the energy required for achieving coplanarity decreases the energy of resonance stabilization, the potential energy of the molecule is increased resulting in a greater bathochromic shift in 4:5-dimethylchrysene in comparison with the isomeric dimethylchrysenes which were examined by Jones.[25]

The spectrum of 3:12-dimethoxydibenzanthrone (IX) shows a small bathochromic shift and a considerable decrease in the intensity of maximum absorption in comparison with dibenzanthrone. In the case of 16:17-dihydroxy- and dimethoxydibenzanthrone, the decrease in the intensity of maximum absorption has been associated with the steric hindrance between

(IX)



(XI)

the vicinal substituent groups; but no such hindrance occurs in the 3:12-dimethoxy compound, and the decrease in the intensity of absorption must be due to the specific effect of substitution in the 3- and 12-positions. Fig. 3 shows the absorption spectra of benzanthrone and 9-methoxybenzanthrone (XI). Here again the methoxy substituent effects a bathochromic shift of the benzanthrone spectrum, simultaneously with a considerable decrease in the intensity of maximum absorption.

In connection with the present study of dibenzanthrone and its derivatives the spectra of the 3:3′-and 4:4′-dibenzanthronyls (XII and XIII) were determined (Fig. 4). There is a remarkable degree of resemblance between the spectra of the 3:3′- and 4:4′-derivatives; comparing them with benzanthrone there is no change at all in the nature of the curve and the

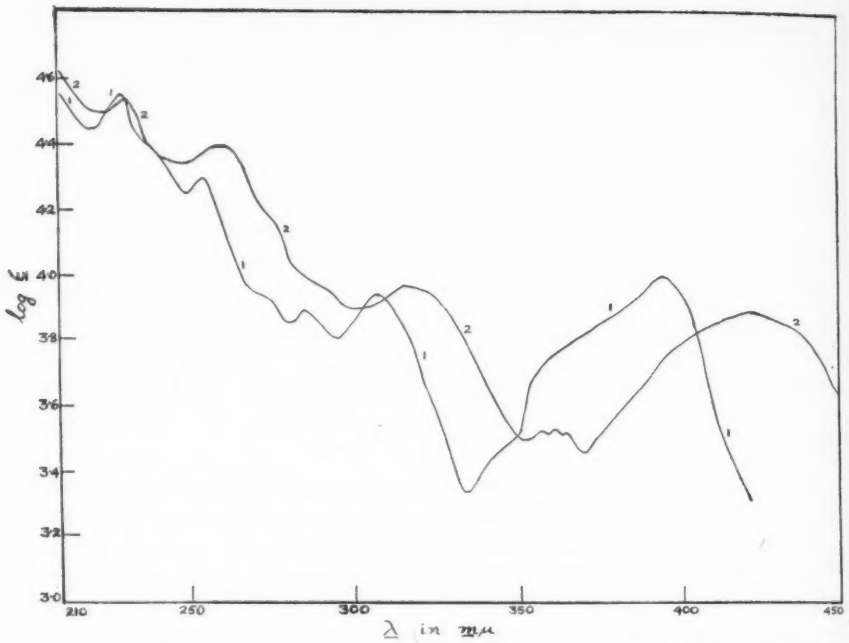


FIG. 3. Absorption spectra of (1) benzanthrone; and (2) 9-methoxybenzanthrone in ethanol.

bathochromic shift with respect to benzanthrone is of the order which an alkyl substituent may effect. A comparison of the intensities of the absorp-

(XII)

(XIII)

tion maxima indicate that the values of benzanthrone have been approximately doubled. The complete similarity between the spectra of benzanthrone and the two dibenzanthronyls indicates that there is no new chromophoric system formed and that there are no possibilities of extended

conjugation across the C—C bond connecting the two benzanthronyl residues because of the effect of steric hindrance of the hydrogen atoms in the 4:4′ or 3:3′-positions. These two dibenzanthronyls can be considered to be derivatives of 1:1′-dinaphthyl which is known to exhibit steric hindrance due to the 8:8′-hydrogen atoms interfering with each other.[20]

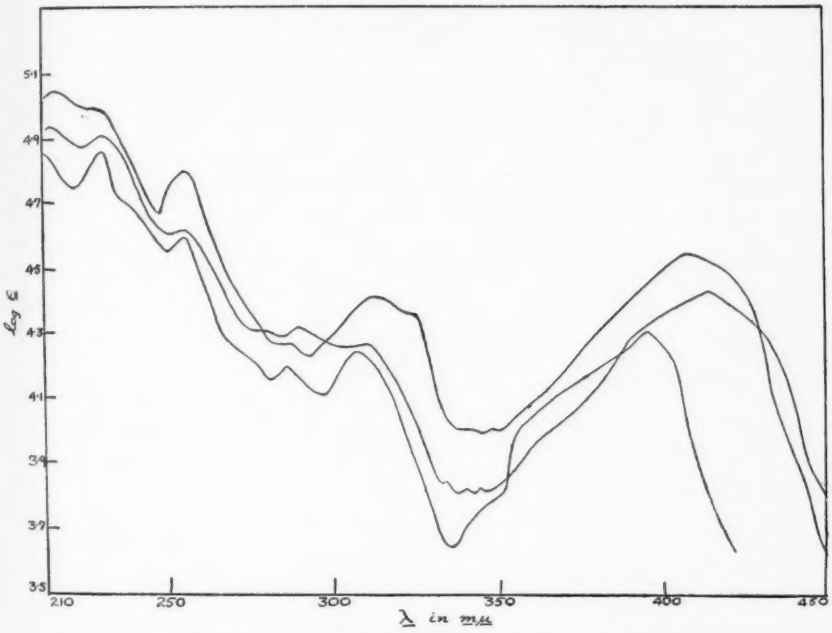


FIG. 4. Absorption spectra of (1) benzanthrone ($E\times2$); (2) 3:3′ dibenzanthronyl; and (3) 4:4′ dibenzanthronyl in ethanol.

EXPERIMENTAL

All the compounds, except benzanthrone for which the spectrum was taken from Friedel and Orchin,[27] were kindly supplied by Dr. P. N. Pandit of this laboratory, and were reported by him.[28] Dibenzanthrone and its derivatives were found to be homogeneous when chromatographed on a column of cellulose powder in the form of their leuco salts, obtained by reducing with tetraethylenepentamine and sodium hydrosulphite. 9-Methoxybenzanthrone and 3:3′- and 4:4′-dibenzanthronyls were found to be homogeneous when their benzene solutions were chromatographed on alumina.

o-Chlorophenol (I.C.I.) was distilled and the fraction boiling between 175–76° was redistilled twice before use. This was found to be transparent

in the ultraviolet region beyond 330 $m\mu$. Absolute ethanol (Government Central Distillery, Nasik Road) (1 l.) was refluxed with silver nitrate (5 g.) and potassium hydroxide (10 g.) for 24 hours and distilled. The fraction boiling at 78° was collected and was found to be transparent beyond 210 $m\mu$.

The absorption spectra were all determined on a calibrated Beckmann Model DUV spectrophotometer. The spectra of dibenzanthrone and its derivatives were determined in *o*-chlorophenol, and because of the low solubility of these compounds, the values for optical density obtained were all below 0·3 with a 5 cm. cell. Saturated solutions of 3:3′- and 4:4′-dibenzanthronyls were prepared and the spectra determined by taking density readings with both 1 cm. and 5 cm. cells. The concentrations of 9-methoxybenzanthrone in alcohol were so chosen that density readings within 0·4 to 0·8 were obtained using a 1 cm. cell.

SUMMARY

The absorption spectra of dibenzanthrone, 16:17-dihydroxydibenzanthrone, 16:17- and 3:12-dimethoxydibenzanthrone have been determined in *o*-chlorophenol. The bathochromic shift of the dibenzanthrone spectrum on substitution of two methoxyl groups in the 16:17-positions of dibenzanthrone is ascribed to the over-riding tendency of the dibenzanthrone ring system to remain planar and hence force the methoxyl groups also to be coplanar with the ring system.

The absorption spectra of 3:3′- and 4:4′-dibenzanthronyls have been reported and discussed.

ACKNOWLEDGMENT

We are indebted to the Council of Scientific and Industrial Research for a fellowship awarded to one of us (N.R.R.).

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ENERGY RESPONSE OF SOME INORGANIC SCINTILLATORS

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Abstract

It is known that densely ionizing particles give rise to a non-linear energy response in organic crystals, while in inorganic crystals in general the light output is proportional to the energy absorbed so that there is no difference between the intrinsic efficiencies for α-particles and γ-ray excitation. The study of some inorganic silicate scintillators reported here shows, however, that they resemble the organic crystals in their non-linear energy response. Contrary to the behaviour of organic scintillators, prolonged α bombardment does not produce any perceptible change in the fluorescence efficiency of these scintillators. The non-linear energy response of these silicates is not explainable by the mechanism of scintillation hitherto proposed.

The number of photons given out in a scintillation caused by an ionizing particle is not simply proportional to the energy lost by the particle. In this respect there is a difference between the behaviour of inorganic and organic phosphors and this arises because of the difference in the mode of energy transfer inside the phosphors. The linearity of energy response is better in the case of inorganic crystals and there is in general no difference between the intrinsic efficiencies for α-particles and γ rays.[1, 2] This is so because the energy transfer process usually involves the motion of charged particles namely, the excited electrons and their vacancies or positive holes. In organic crystals and liquids the intensity of scintillation is in general not proportional to the energy absorbed and as such they are far less efficient for the detection of heavy particles than for electrons or γ rays.[3, 4] Bowen and his collaborators[5] have studied the luminescence of naphthalene crystals with small impurities of anthracene (both of which fluoresce) when excited by ultraviolet light. The observed luminescence emission was found to be mainly characteristic of anthracene molecules and of very much greater intensity than would arise from the absorption in only these molecules. A similar effect has also been observed by Kallman and Furst for solutions

of fluorescent molecules in organic liquids.[6] An explanation of this effect and the fast rise time of the scintillation pulses has been given on the ' exciton ' energy transfer process where the energy is transferred from one molecule of the lattice to another until the ' exciton ' is trapped at an impurity molecule where its energy can be converted into a luminescence photon. There is no charge transport as in transfer processes of inorganic crystals. In fact

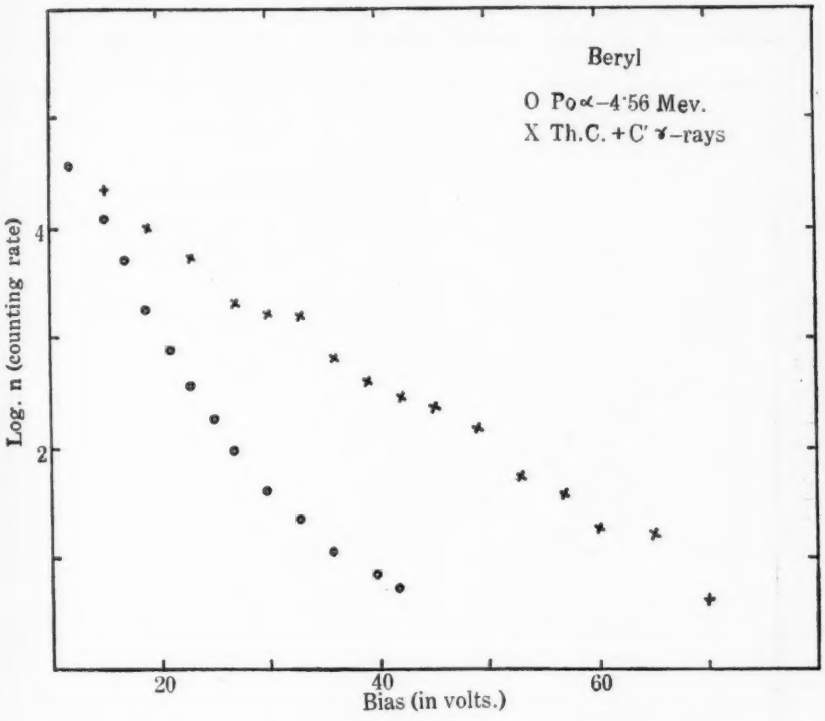

FIG. 1

the presence of electrons may be deleterious since the resulting ionized molecules will also trap the energy and dissipate it non-radiatively. Birks[7] has used the above ideas to explain the non-linear energy response of organic crystals and liquids. According to him the passage of a heavily ionizing particle produces a local concentration of damaged molecules along its path, which act as quenching agents for the ' excitons '. The experimental response ratios seem to agree with the predicted values. This is generally true of all organic crystals and liquids.

The deterioration of organic crystals under prolonged α bombardment has also been explained with the help of exciton theory.[8] It has been observed that the light intensity in organic crystals goes on decreasing with α bombardment, the relative amplitude $\frac{I}{I_0}$ decreases as

$$\frac{I}{I_0} = \frac{1}{1 + AN}$$

where N is the total number of α-particles/cm.^{2} striking the crystal and A is a constant. If q_0 is the original number of molecules of anthracene/cm.^{2}

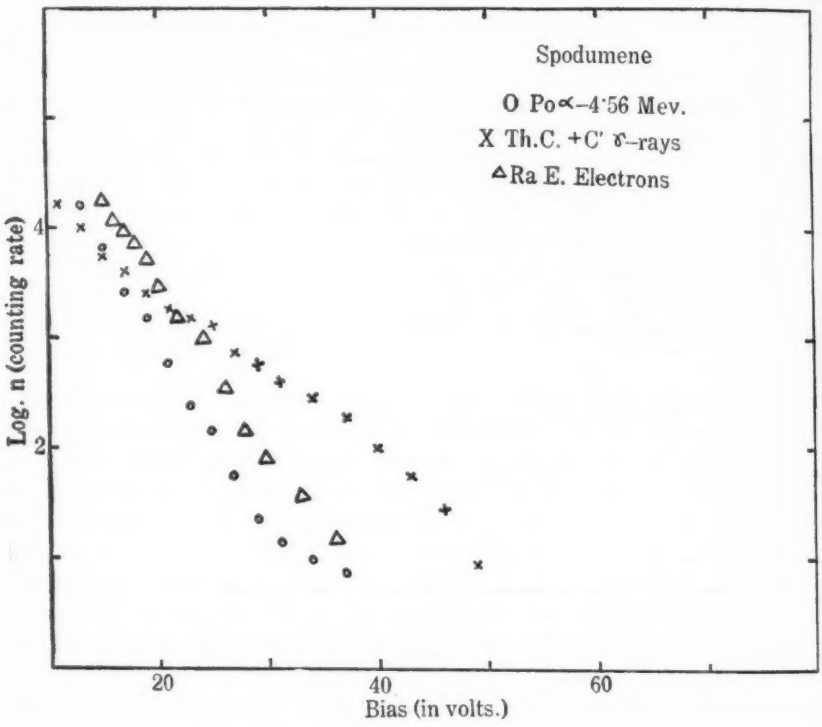

FIG. 2

in the irradiated volume, and each α-particle damages p molecules, then a concentration of damaged molecules, after Nα-particles/cm.^{2} have struck the crystal, will be $x = \exp.\left(\frac{pN}{q_0} - 1\right)$ molecules per undamaged molecule of anthracene. If a damaged molecule has an exciton capture probability

k relative to an anthracene molecule, the relative amplitude of the fluorescent anthracene radiation will be

$$\frac{I}{I_0} = \frac{1}{1+kx} = \frac{1}{1+kp\dfrac{N}{q_0}} \left(\text{For small values of } \left(\frac{pN}{q_0}\right) \right)$$

The following is a study of the linearity of energy response of some natural inorganic scintillators.

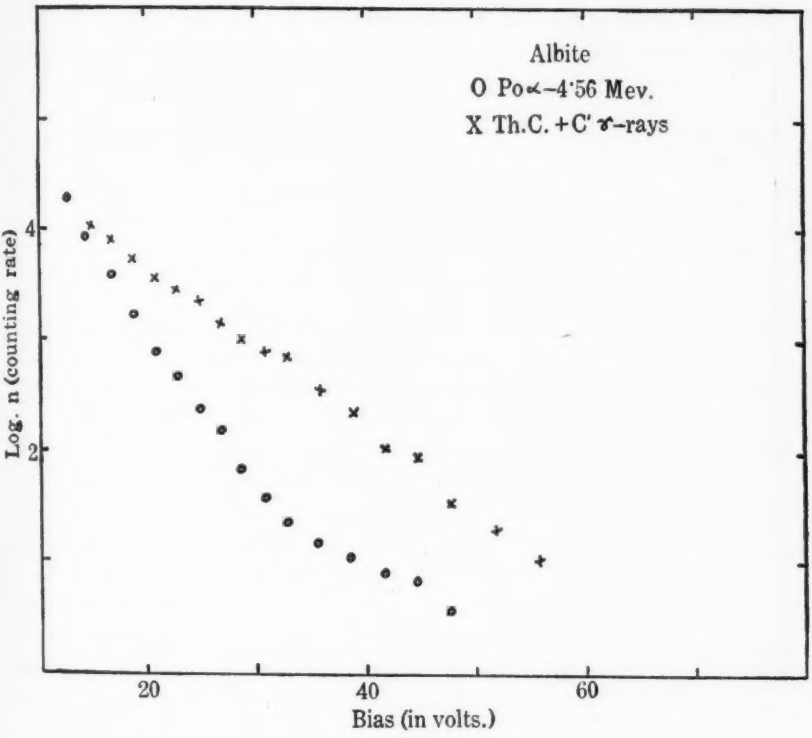

FIG. 3

METHOD AND APPARATUS

The detection apparatus consisted of an E.M.I. type 6262 fourteen stage photomultiplier tube with a 6AK5 cathode follower stage serving as head amplifier. The pulses were fed into a Jordan and Bell type linear amplifier and were counted with a scaler-discriminator arrangement.

The P.M. tube was operated at — 800 V. supplied from a stabilised power supply. The background due to the P.M. tube noise was extremely

low at this voltage. The crystals were directly cemented to the P.M. tube and a spherically polished aluminium surface was used as reflector. The crystals studied were:—

(1) Anthracene (1 cm. × 1 cm. × 1 cm.) was a single colourless crystal supplied by the Larco Nuclear Instruments Co.

(2) Beryl [$Be_3 Al_2 (SiO_3)_6$]. Several samples of beryl were studied. Natural crystals of beryl are found in different colours ranging from emerald

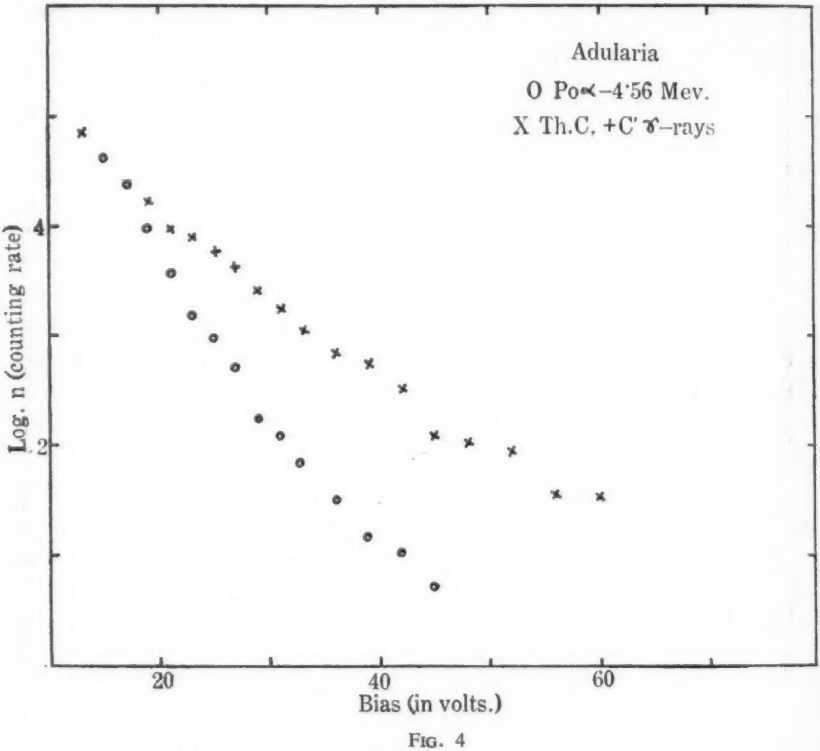

FIG. 4

green, light blue, yellow to colourless. The qualitative behaviour was found to be the same in all the samples. The emission of light was maximum in the colourless samples. Detailed measurements were taken on a thin flat colourless sample. A synthetically grown crystal of beryl was also found to have the same behaviour.

(3) Spodumene [Li Al $(SiO_3)_2$] a translucent flat crystal white in colour.

(4) Albit (Na Al $Si_3 O_8$) a small colourless transparent crystal.

(5) Adularia ($K\,Al\,Si_3\,O_8$) a flat colourless clear sample.

(6) *Diamond.*—The crystals tried were industrial unpolished flat pieces. The samples were also tested for their conduction counting properties with the usual conventional arrangement. No response was observed for α-particles or γ rays.

An integral bias spectrum for each crystal using the above sources was taken. The maximum pulse height was estimated by extrapolating a log plot of the counting rate against bias, Figs. 1–4. Relative figures for all the crystals were obtained for the ratio R (the light output for 4·56 MeV α-particles and 2·62 MeV γ rays). Values of R are shown in the table:

TABLE I

	Beryl	Spodumene	Albit	Adularia	Diamond
R	0·54	0·59	0·59	0·62	1·36

PROLONGED ALPHA BOMBARDMENT

The top surface of a (1 cm.$\times$1 cm.) anthracene crystal was bombarded by a 10 m.c. Po-α source kept 0·8 cm. above the crystal. Periodically the strong source was removed and the counts at fixed biases were taken with a weak collimated Po- α source. After ten hours of bombardment (approx. 5×10^{12} α-particles) the pulse heights had decreased by more than 90 per cent., in agreement with other observers.[8,9]

A thin flat crystal of beryl was also bombarded by α-particles as described above. No perceptible change in pulse height seems to have occurred even after irradiation with 10^{13} particles. This is in general true of all inorganic crystals.[9]

It is clear from Table I that, unlike the general behaviour of inorganic scintillators, these silicates seem to resemble the organic crystals in their higher efficiency for γ rays as compared to α-particles. On the other hand the prolonged α-bombardment failed to show any perceptible change in the fluorescence efficiency contrary to the observations on organic crystals. Though no detailed measurements of the rise times of these crystals have been made, qualitatively the rise times do not appear to be as fast as the organic scintillators and seem to be of the same order as that of diamond. Many interesting peculiar optical properties have been observed for these complex silicate crystals and in order to explain the absorption properties of zinc silicate with an impurity of manganese an exciton transfer process

has been suggested by Bulter.[10] It appears that the differences in the scintillating properties of inorganic crystals is closely connected with the molecular binding forces and their crystal structure.

My sincere thanks are due to Prof. H. J. Bhabha for his kind interest in this work and I am grateful to Dr. R. Ramanna for helpful discussions throughout the course of this work. I also wish to express my thanks to Prof. P. K. Kitchlu, Delhi University, Mr. R. V. Mandre and Dr. Jagdish Shankar and Messrs. Diamond Corporation of India Ltd. for supplying the crystals.

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Note Added in Proof.—Recently W. T. Link and D. Walker (*Proc. Phys. Soc.*, 1953, August 767) have noted a non-linear relation between the light output and particle energy in the case of KI (TI) at high energies. According to them this is consistent with the picture of a limited number of luminiscent centres in the crystal (I. Broser and R. Warminsky, 1951, Z.*Naturforsch.*, 6 *a*, 85., G. T. Wright and G. F. J. Garlic, 1953, *Brit. J. Appl. Phys.* in the press). When the density of ionizing electrons becomes very large, the number of electrons which can be captured by luminiscent centres tends to a limit. The small pulse heights due to α-particles reported in our paper can be explained on the picture of limited number of luminiscent centres.

SOME INTERESTING ATMOSPHERIC SOUNDINGS OF PRESSURE AND TEMPERATURE MADE WITH VÄISÄLÄ RADIOSONDES AT AHMEDABAD

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1. Introduction

Various types of radiosondes have been devised in recent years for ærological soundings. The authors had opportunity to work with two such types in the last two years (1950–52). The Fan-type radiosondes, developed by the India Meteorological Department, were in use in this laboratory for regular, day-to-day observations. About 120 successful ascents were also made with the Finnish instruments of Vilho Väisälä.

Of these latter ascents, a few were conducted with a view to compare the performances of the two kinds of radiosondes (Fig. 1). Some were planned in situations of interesting weather. Thirty-five of them were swarmed into a period of 13 days in April 1952 in an attempt to investigate the question of the diurnal variation of temperatures in the upper atmosphere.

We report and discuss the results of these ascents in this paper.

2. The Väisälä Radiosonde

The meteorological units in the Väisälä radiosonde are an aneroid capsule, a bimetal strip and a stretched piece of hair to measure respectively the pressure (P), temperature (T) and relative humidity (H).

These units are linked to the movable plates of separate parallel-plate condensers, and the variations in the meteorological elements are converted into variations of capacitances.

The meteorological condensers are switched in sequence into the tank-circuit of the radiosonde oscillator by means of a rotatory switch operated by a wind-mill. The same switch also connects two other fixed reference-condensers C_K and C_k into the circuit.

The radiosonde oscillator has a frequency range of 24–26 Mc/S within which all the transmission frequencies controlled by the 5 condensers lie.

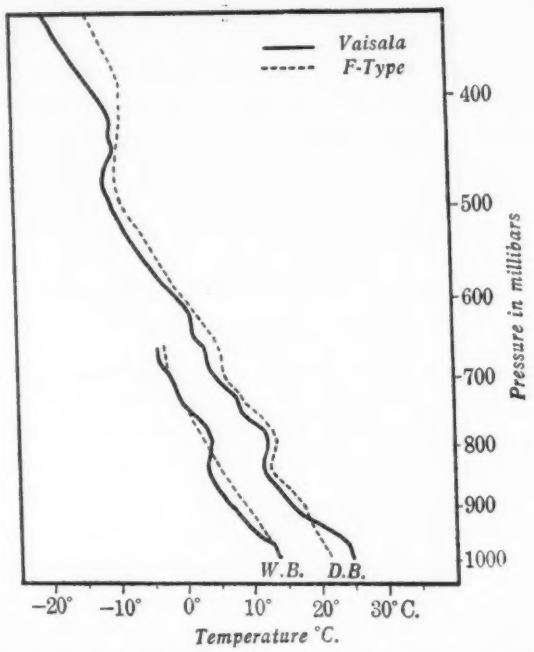

FIG. 1. Comparison of the performances of the Väisälä and the F-type radiosondes. The Väisälä instrument was launched at 1800 hrs. on 21-1-51 and the F-type instrument one hour later.

The ground equipment is a 6-valve superheterodyne set. By means of a semi-circular tuning condenser, conveniently operated by hand, the local oscillator of this set is beated with the transmissions of the air-borne radiosonde. The beats are audible as fast, short squeaks at 5 different positions of the tuner. By pressing a stylus attached to the tuner, these 5 positions are punched on a recording-paper wound on a clock-driven drum.

Full details of the instrumental calibration are given in Väisälä's "Handbook of Sounding."[3] There it is shown that the value of the particular meteorological element P, T or H is proportional to $\frac{C_K - C_m}{C_K - C_k}$ where C_K, C_K and C_m are the instantaneous values of the two reference condensers and the meteorological condenser respectively. Since values of C_m are measured in units of $C_K - C_k$, it is seen that wholesale shifts in wavebands that may occur due to various causes during flight or calibration do not affect the accuracy of measurements.

Fig. 2 is a reproduction of the radiogram obtained at Ahmedabad on 18–4–1952. The dotted traces corresponding to P, T and H are shown

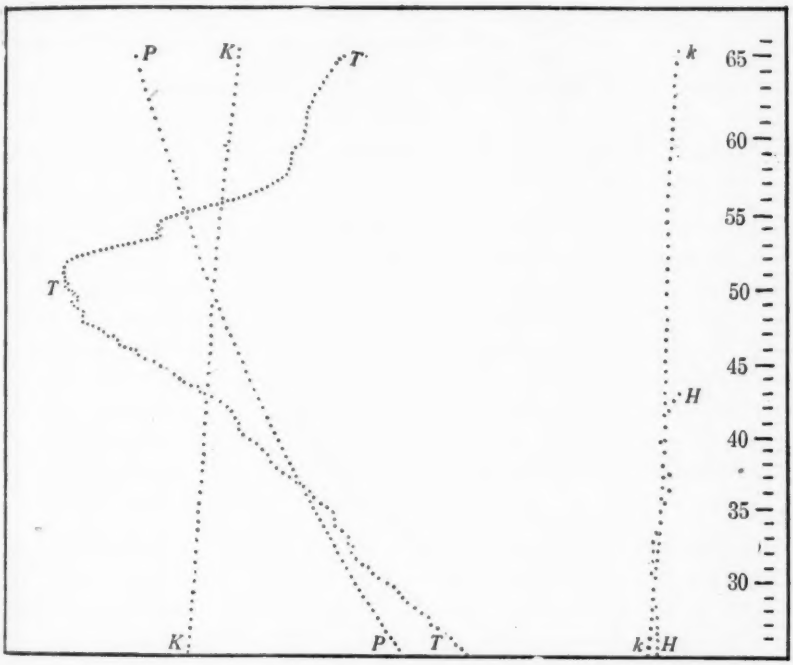

FIG. 2. Reproduction of a portion of the radiogram of the afternoon ascent on 18–4–52 In the natural size of the record the distance between KK and kk is nearly 100 mms.

along with the parallel curves obtained for K and k. Numbers on the right-hand side of the record give the time in minutes after the release of the radiosonde.

3. SOUNDINGS OF 18–4–1952 AND 19–4–1951

We describe below a few salient points connected with two particular soundings selected from our collection. The first of these was taken on the afternoon of 18–4–1952. The radiosonde was held in position in a cage and the transmitter-battery kept safe from tilting so that reliable measurements of temperature and pressure could be obtained during the ascent of the instrument till the burst of the balloon, and also during its subsequent fall. Since no parachute was attached, however, the ascent and the descent took place at appreciably different speeds.

A portion of the radiogram of this sounding has already been presented in Fig. 2. Fig. 3 gives the height-temperature diagram evaluated from this radiogram. On the same figure is also plotted the smoothed time-height curve of the balloon used. Temperatures measured during the

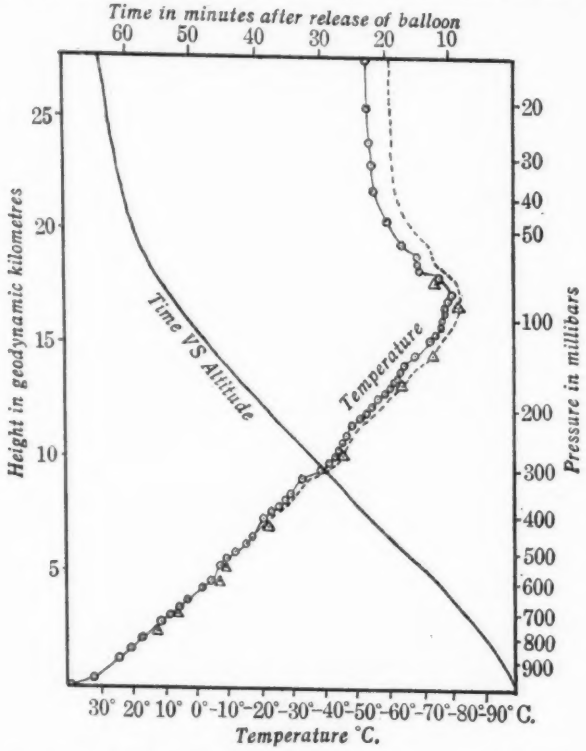
Time in minutes after release of balloon
60 50 40 30 20 10
Height in geodynamic kilometres
25 20 15 10 5
Time VS Altitude
Temperature
Pressure in millibars
20 30 40 50 100 200 300 400 500 600 700 800 900
30° 20° 10° 0° -10° -20° -30° -40° -50° -60° -70° -80° -90° C.
Temperature °C.

FIG. 3. Height-temperature diagram of the ascent on 18–4–1952.

ascent of the instrument are marked by circles, and those obtained during its descent by triangles.

As the sounding was made in the afternoon, upper-level temperatures could be subject to considerable " radiation-error ". Väisälä[3] has discussed a method of correcting for this error on the following main assumptions: (1) Below 500 mb. it is negligible. (2) Above 500 mb. and below 200 mb. it increases linearly. (3) Above 200 mb. its value at any level is a function of certain instrumental constants (which can be measured in the laboratory) and on the momentary values of the height-angle of the Sun and the rate of ascent of the balloon.

The dotted curve in the diagram, running alongside the plot of measured temperatures gives, according to Väisälä, the correct temperatures at the appropriate levels. Differences between measured and corrected values are seen to be of the order of 3° C. at 200 mb. and 8° C. at 15 mb.

Other features of interest are:—

(1) Temperatures obtained at a particular level during the ascent and the descent of the radiosonde are different.

(2) The rate of ascent of the balloon increases abruptly at the stratosphere.

Some of the observed differences of temperature between ascent and descent can result from the sluggishness of response of the thermometric element. In an atmosphere in which temperature decreases with height, the indicated temperature will be, due to thermometric lag, *higher* than the actual temperature during the ascent and *lower* during the descent. This lag will increase with reduced air-density so that the difference between the indicated temperatures will also increase with height. Since, in the Väisälä radiosonde, telemetering of temperature is done without any mechanical loading, the dimensions of the bimetal, and consequently its lag-coefficient, are reduced to a minimum.

Most of the observed differences of temperature is thus due to the difference in the magnitudes of the radiation error inherent in the two measurements. The amount of solar radiation falling on the instrument is smaller at the later time of the descent, while the ventilation given to it is greater. Thus the radiation error is smaller during the descent. It is an interesting coincidence that Väisälä's corrected temperature curve falls roughly along points obtained during the descent.

Part of the stratospheric increase of the rate of ascent of the balloon is probably artificial, and is the result of pressure and temperature errors reflected in the computed values of height. However, it may be noted that the decrease of kinematic viscosity μ/ρ in the stratosphere—the appropriate value of μ is the 'eddy viscosity' in the troposphere and the much smaller 'molecular viscosity' in the stratosphere—can bring about such an increase. The decreases in ascensional rates that are sometimes observed in the stratosphere are mostly due to balloon leakage.

The second sounding that we discuss was made at 1900 hrs. (I.S.T.) on the 19th of April 1951. On a comparison of the corresponding radiogram (Fig. 4) with a normal sounding-record (Fig. 2), we find that the

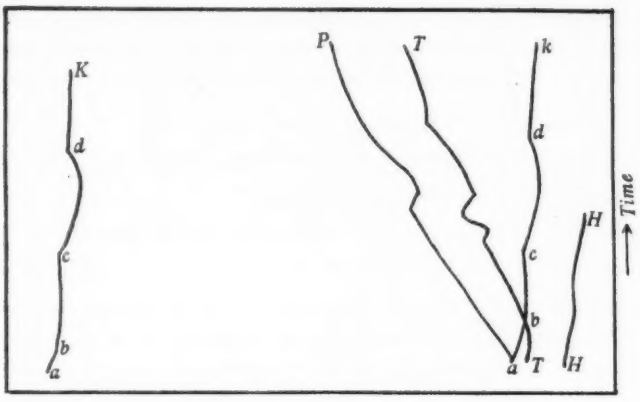

FIG. 4. Radiogram of 19–4–1951.

curves obtained in this case for the constant condensers K and *k* are more complex than usual. This may be accounted for in two ways: (1) The constant condensers might have suffered injuries between calibration and ascent. Against this it has to be observed that the control-readings, taken at the field prior to the sounding, did not reveal unreasonable calibration-shifts in pressure of temperature. (2) There was a wholesale wave-band change in the course of the sounding. The close parallelism between the curves for K and *k* appears to suggest such a wave-band drift. It does not in any way affect the accuracy of measurement.

We have evaluated the radiogram on the latter assumption. The resulting time-height curve of the balloon is given in Fig. 5. According to this diagram the balloon had an average rate of ascent of 18 km./hr. upto 2·8 km. Between 2·8 km. and 4·2 km. the rate of ascent increased to a value of nearly 30 km./hr. At the latter height the balloon encountered a strong, descending current which dragged it down a distance of 250 meters in approximately 2½ minutes. The balloon resumed its ascent, thereafter, at its initial rate of 18 km./hr.

In Fig. 5 is also plotted the wind-speeds obtained from pilot-balloon observations at 1430 hrs. at the station meteorological office. Arrows indicate the direction of the wind. It is significant that the height-interval in which the radiosonde balloon experienced changes in rate of ascent coincided with the region of maximum vertical wind-shear.

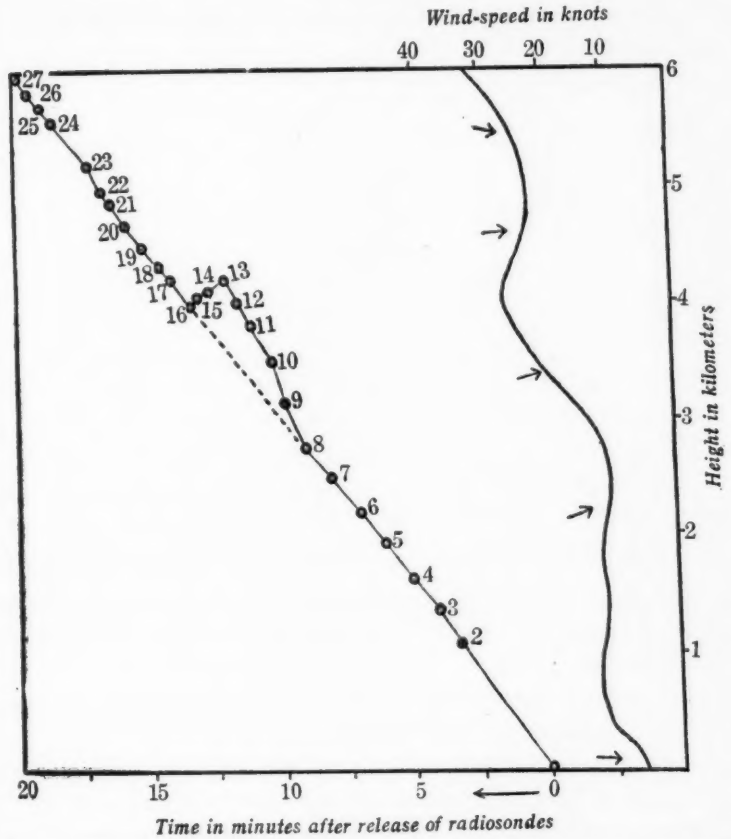

FIG. 5. The time-height curve of the radiosonde balloon on 19–4–1951. The wind-speeds as obtained from pilot-balloon observations are also plotted. Arrows indicate wind-direction.

In Fig. 6 the ærogram of this sounding has been put in juxtaposition with those obtained for the soundings made on the previous and the succeeding days. The same ordinal numbers are used in Figs. 5 and 6 to denote a particular point with the co-ordinates (p, T).

The day of the sounding under discussion was more gusty than usual. There was 2/10ths of altocumulus cloud in the morning, but the sky was clear at the time of ascent. The night-temperatures fell by 4° F. The synoptic chart did not locate any front in this region.

It is concluded that the radiosonde balloon might have been trapped in a localised eddy formed in an unstable region of considerable wind-shear.

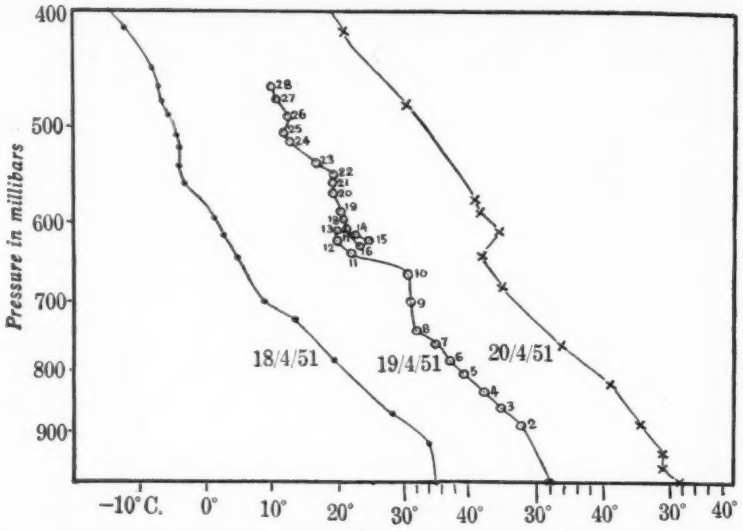

FIG. 6 Aerograms of the radiosonde ascents on 18–4–1951, 19–4–1951 and 20–4–1951.

Mainly because of the absence of the moisture in the atmosphere, however, the vertical movements indicated by the radiosonde failed to produce much apparent " weather ".

4. TEMPERATURE-STRUCTURE OF THE LOWER ATMOSPHERE AND THE NATURE OF THE 'TROPOPAUSE-TRANSITION'

One of the commendable features of the Väisälä radiosonde is the fine-grained continuity of the measurements that can be made with it. This enables it to investigate certain problems of peculiar meteorological interest. We cite below two examples:—

(1) Fig. 7 is drawn as the average of all the observations obtained in the month of April. This figure illustrates the typical nature of the diurnal variation of temperature that is generally noticed in the surface layers of the atmosphere. In the afternoon, intense insolation of the ground produces a shallow layer (approximately 200 metres in thickness) of super-adiabatic lapse-rate. Turbulent transfer of heat, however, tends to destroy this unstable condition. By evening, a weak inversion starts to form at the surface. Helped by radiational cooling at night, this inversion builds up to a depth of 300 to 400 meters just before sunrise. It is subsequently " burnt off " due to heating from the bottom. It can be seen from the figure that difference between the afternoon and the morning temperatures,

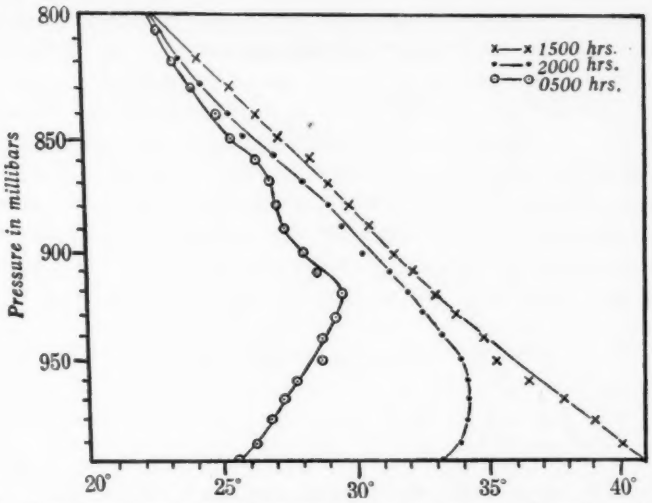

FIG. 7. The diurnal variation of temperature in the month of April at Ahmedabad. The curves are drawn as the average of observations made three times a day with Väisälä radiosondes.

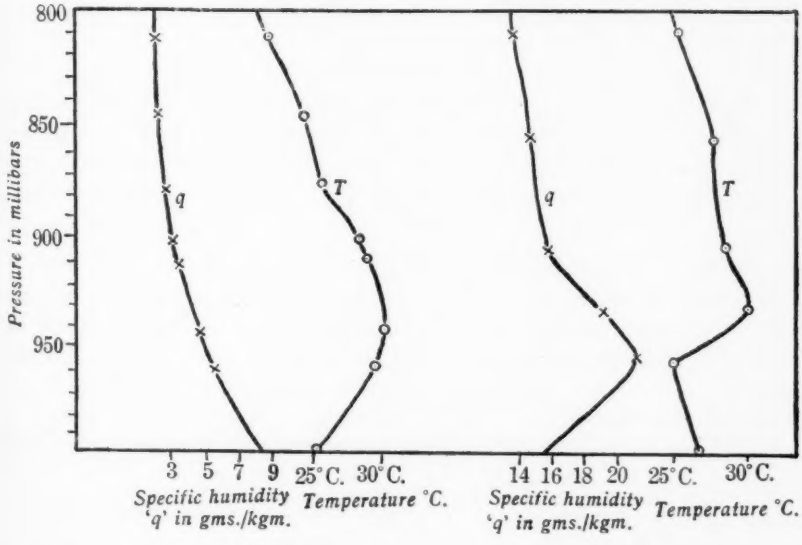

FIG. 8. Temperature and humidity profiles in the early mornings (0500 hrs.) of two individual days in April in Ahmedabad.

which represents approximately the amplitude of the diurnal variation, decreases rapidly with height and vanishes nearly at 800 mb. (2 km.). The inversions that form near the surface of the ground at night often act as " radio-ducts " and are known to be responsible for the " unorthodox " propagation of high-frequency electromagnetic radiation. Accurate profiles of temperature and humidity are valuable in the study of the conditions for such propagation. Fig. 8 gives such profiles for a ' surface-duct ' and an ' elevated-duct ' observed on two individual days in April.

(2) In Fig. 9 are given some beautiful patterns obtained for the temperature-structure in the transitional region between the troposphere

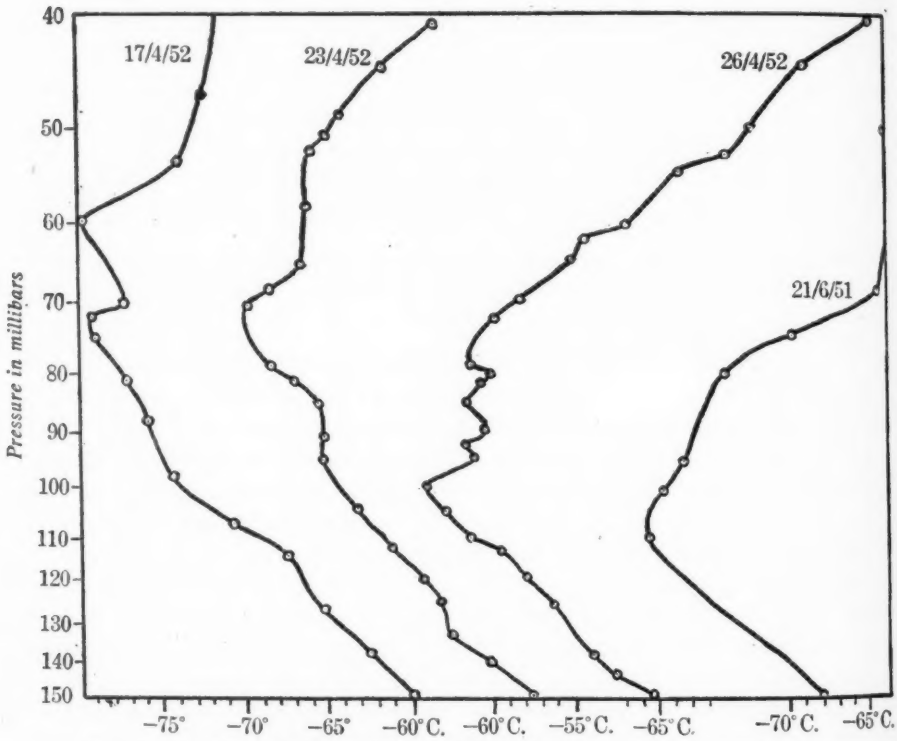

FIG. 9. The detailed structure of the transition between the troposphere and the stratosphere at Ahmedabad obtained from Väisälä ascents.

and the stratosphere. Out of the four soundings that are presented in this diagram, three were made in summer (April) and one at the time of onset of the active monsoon (June). The variations in the temperature-profiles

accompanying different types of weather, particularly in conditions like the western disturbances that travel across N.W. India in winter, is a study that remains to be carried out by means of high-level soundings more regular and numerous than what has been possible to report in this paper.

5. The Diurnal Variation of Temperature in the Upper Troposphere

In connection with the time-variation studies of cosmic-rays, this laboratory was interested in the nature of the diurnal variation of temperature in the upper troposphere and the lower stratosphere. With a view to examine this question, about thirty-five ascents were spaced in a period of thirteen days in the month of April 1952. Three ascents were made in a day, one just prior to sunrise (0500 hrs.), one well after sunset (2100 hrs.) and one at the time of maximum temperature at the ground (1500 hrs.). Nearly the same type of surface weather persisted throughout the period.

The results of these ascents are summarised in Fig. 10 and Table I.

Fig. 10 is a time-section of the ascents. The time-axis runs from right to left. Each day is marked by its appropriate date. The ordinates give the pressure-levels. Each ascent is represented by a vertical line erected at the correct time and rising upto its ceiling-height. The smoothed lines in the figure are the isotherms drawn at intervals of 5° C. A scrutiny of this diagram appears to suggest that the day-to-day variations of temperature in the upper troposphere are much more pronounced than what are observed in the surface layers. The shapes of the isotherms make it reasonable to say that there are damped temperature waves with a period of approximately three to four days at these heights. The amplitudes of these waves increase rapidly in the region of 200 mb. There is also some evidence for the transport of very cold (— 80° C.) pools of air near the tropopause in the form of large-sized eddies.

Table I is prepared to bring out the observed nature of the diurnal variation of temperature at the upper levels. For each isobaric surface, the measured differences between the morning and the afternoon temperatures ($T_M - T_A$), the afternoon and the evening temperatures ($T_A - T_E$), and the evening and the next morning temperatures ($T_E - T_M$) are given in this table. The means of these differences as well as their standard deviations are also given. Much weight, however, cannot be attached to these values as the number of observations available is not sufficiently large.

The available results point out that *significant* and *regular* diurnal variation of temperature occurs only in the turbulent, surface layer of the

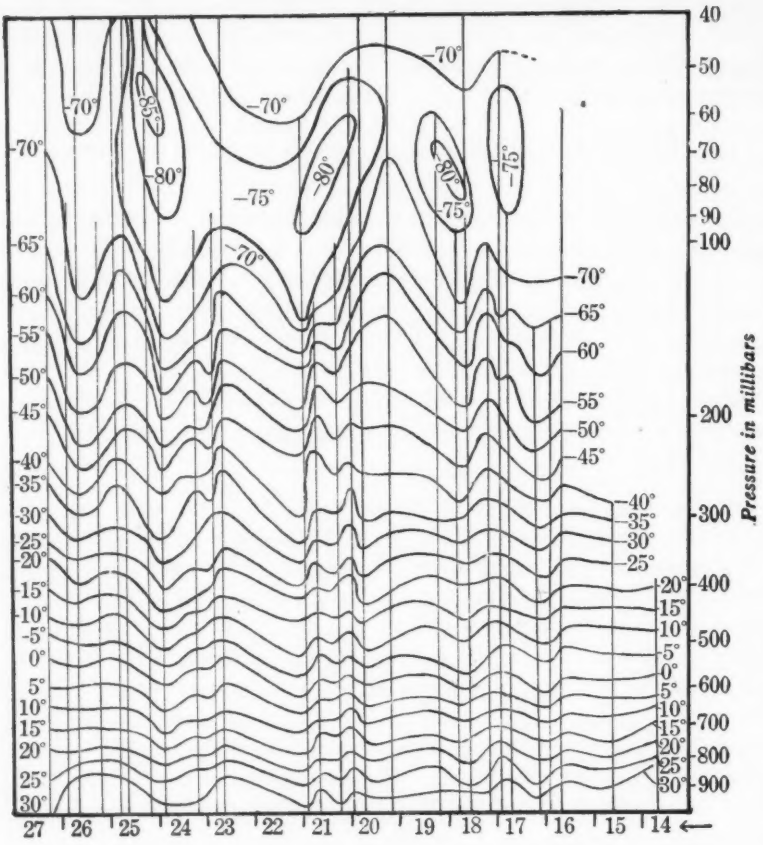

FIG. 10. Time-section of the serial ascents taken at Ahmedabad in April 1952.

atmosphere (upto 800 mb.). We have discussed the nature of this variation in Section 4. In the higher levels, though large changes of temperature are measured by the radiosondes in the course of a day, these variations are not shown to be statistically significant.

Many workers have attempted to detect the magnitude of the diurnal variation of temperature in the upper troposphere and the lower stratosphere by analysis of a large number of radiosonde ascents. Recently Kay[2] has discussed the results of nearly 11,000 ascents made in the course of four years at four stations in England. His main conclusions are (1) the temperature differences indicated by ascents taken immediately after sunset

TABLE I

Measured Temperature-differences (in ° C.) between morning and afternoon ($T_M - T_A$), afternoon and evening ($T_A - T_E$) and evening and the next morning ($T_E - T_M$) at specified isobaric levels

Ground			900 mbs.			800 mbs.			700 mbs			600 mbs.		
$T_M - T_A$	$T_A - T_E$	$T_E - T_M$	$T_M - T_A$		$T_E - T_M$	$T_M - T_A$	$T_A - T_E$	$T_E - T_M$	$T_M - T_A$	$T_A - T_E$	$T_E - T_M$	$T_M - T_A$	$T_A - T_E$	$T_E - T_M$
..	+ 7·5	+ 9·5	..	+0·4	+1·4	..	+2·9	−0·6	..	+3·7	−1·3	..	+3·7	−0·2
−15·5	+ 4·5	+10·0	−4·0	+3·0	+6·5	−2·7	−2·8	0·0	−2·7	−0·6	+0·6	−4·9	−0·7	−0·3
−13·5	+ 5·5	+ 7·0	+0·9	+0·6	−2·0	+7·7	−1·7	−2·5	+3·6	−1·6	−1·4	+4·9	−3·7	−0·7
−13·0	+ 6·0	+ 8·0	+0·2	−0·5	+1·7	−2·0	−3·1	+1·0	+2·1	−4·4	+1·9	+2·0	−4·4	+4·1
−17·2	+10·2	..	−2·7	+4·4	..	+0·4	+4·0	..	−0·3	+5·6	..	−1·8	+4·5	..
..	+ 8·0	+ 6·0	..	+4·1	+3·0	..	+4·2	−0·7	..	+2·2	+0·8	..	+2·6	0·0
..	..	+ 4·0	..	..	−1·0	..	..	−3·8	..	..	−4·0	..	..	−2·9
−16·0	+ 7·0	+ 9·7	−3·1	−1·5	+5·0	−2·7	−0·8	+1·0	−1·2	−0·5	−0·3	−0·8	−1·6	+0·2
−16·2	+ 6·2	+ 9·3	−4·7	+4·4	+0·6	+0·2	0·0	−0·8	0·0	−0·3	−0·2	+0·9	−0·6	−0·4
Mean—														
−15·2	+ 6·8	+ 7·9	−2·2	+1·8	+1·9	+0·2	+0·3	−0·8	+0·3	+0·5	0·0	0·0	0·0	0·0
Standard Deviation—														
1·7	1·7	2·1	2·3	2·4	2·9	3·9	3·0	1·7	2·3	3·2	1·9	3·4	3·3	1·9

TABLE I—(*Contd.*)

500 mbs.			400 mbs.			300 mbs.			250 mbs.			200 mbs.			150 mbs.		
T_M-T_A	$_A-T_E$	T_E-T_M	T_M-T_A	T_A-T_E	T_E-T_M	T_M-T_A	T_A-T_E	T_E-T_M	T_M-T_A	T_A-T_E	T_E-T_M	T_M-T_A	T_A-T_E	T_E-T_M	T_M-T_A	T_A-T_E	T_E-T_M
..	+2·8	−0·3	..	+3·7	+0·2	..	+2·2	−0·4	..	+3·5	−0·3	..	+ 3·5	+1·5	..	+3·3	..
−3·6	−1·1	+2·3	−4·5	+0·2	−0·2	−3·2	−1·5	0·0	−3·5	−1·7	−2·4	−5·5	− 1·5	−1·7	..	+0·5	− 3·0
+3·0	−3·0	−1·0	+1·5	−3·0	−1·3	+6·1	−2·6	+1·0	+6·6	−1·0	−3·0	+6·7	− 3·0	−1·2	+6·5	+0·8	− 5·0
+2·3	−4·0	+2·5	+3·4	−4·4	+2·7	+1·7	−4·0	+4·0	0·0	−2·0	−2·0	+1·7	− 0·5	−1·6	+2·7	−0·6	+ 6·2
−1·7	+4·2	..	−1·4	+5·9	..	−2·4	+4·9	..	−4·0	+5·1	..	−4·9	+11·3	..	−4·0	−9·4	−10·6
..	+4·4	0·0	..	+5·4	−0·3	..	+2·5	−0·2	..	+6·7	−1·5	..	+ 8·2	−2·2	..	+7·1	+ 0·1
..	..	−6·4	..	..	−6·5	..	..	−1·2	..	..	−5·4	..	..	−7·9	..	..	−11·8
−2·2	−2·1	+0·6	−3·7	−2·2	+1·7	−5·5	+1·3	+2·2	−4·8	+0·3	+6·4	−0·2	− 1·9	+6·5	−1·7	+0·5	+ 8·5
+1·3	−0·6	−2·7	+2·4	−1·9	−1·6	+1·5	−2·9	+1·6	+1·6	−2·7	−4·1	+1·8	− 2·8	−7·0	−0·3	+1·1	−13·0
−0·2	+0·1	−0·6	−0·4	+0·5	−0·7	−0·3	0·0	0·9	−0·7	+1·0	−1·5	−1·1	+ 1·7	−1·7	+0·6	+0·4	- 3·5
2·8	3·3	2·9	3·3	4·0	2·8	4·2	3·1	1·7	1·4	3·6	3·6	4·3	5·5	4·5	4·1	4·7	7·6

and just before sunrise are small. The order of magnitude obtained for the nocturnal cooling is about 0°·5 K which agrees with the theoretical value obtained by Gowan and Penndorf on the assumption of radiative equilibrium at these levels. (2) The mean midday-midnight temperature differences are much higher. The diurnal range varies *with the seasons at the same level* and is *inversely proportional to pressure at different levels.* At 100 mb. the daily amplitude is 3° K. in summer and 2° K. in winter. At 50 mb. these amplitudes are doubled. (3) A sudden increase of temperature is observed just after sunrise. A similar fall follows sunset. (4) Differences between day-time observations placed symmetrically about the noon are small. They indicate a maximum rise of 0°·5 K in the afternoon consistent with the magnitude of the cooling at night at these levels.

It has been suggested by Kay that most of these results are explicable as primarily due to inherent errors in radiosonde measurements.

Such errors can be either casual or systematic. Casual errors arise due to lack of strict intercomparability between instruments and the inevitable random-sampling of the non-uniform conditions in the upper atmosphere. They may be effectively eliminated by consideration of a large number of ascents. The most serious systematic errors are (1) errors in pressure-measurements which are of the order of $\pm$ 5 mb. at 25–30 km. and (2) errors in temperature measurements mostly caused by the direct irradiation of the thermometric element by sunlight. The latter error is attempted to be minimised in radiosondes by providing properly designed radiation-shields and having measuring units of small surface area, high reflectivity and low heat-capacity. But a correct evaluation and removal of this error is difficult. Scaling experiments in which the thermometric elements are chosen to have progressively-graded physical properties have been suggested. Brasefield[1] has experimentally studied the dependence of the radiation error on such factors as the geometry of the radiation-shields and the thermal and optical properties of the measuring units. More recently suggestions of indirect methods of temperature determination as from sonic velocity or β-ray absorption measurements have also been made.

With our present knowledge obtained from ærological ascents, it appears difficult to arrive at a definite conclusion about the nature and magnitude of any regular, diurnal variation of temperature in the upper levels of the troposphere.

6. Summary

A brief description of the Väisälä radiosonde is given and its general performance-characteristics discussed. Some results of ascents made at

Ahmedabad with this type of instrument in the last two years are presented. The question of the diurnal variation of temperature in the upper atmosphere is examined with reference to the serial ascents made in the month of April 1952.

7. ACKNOWLEDGEMENT

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